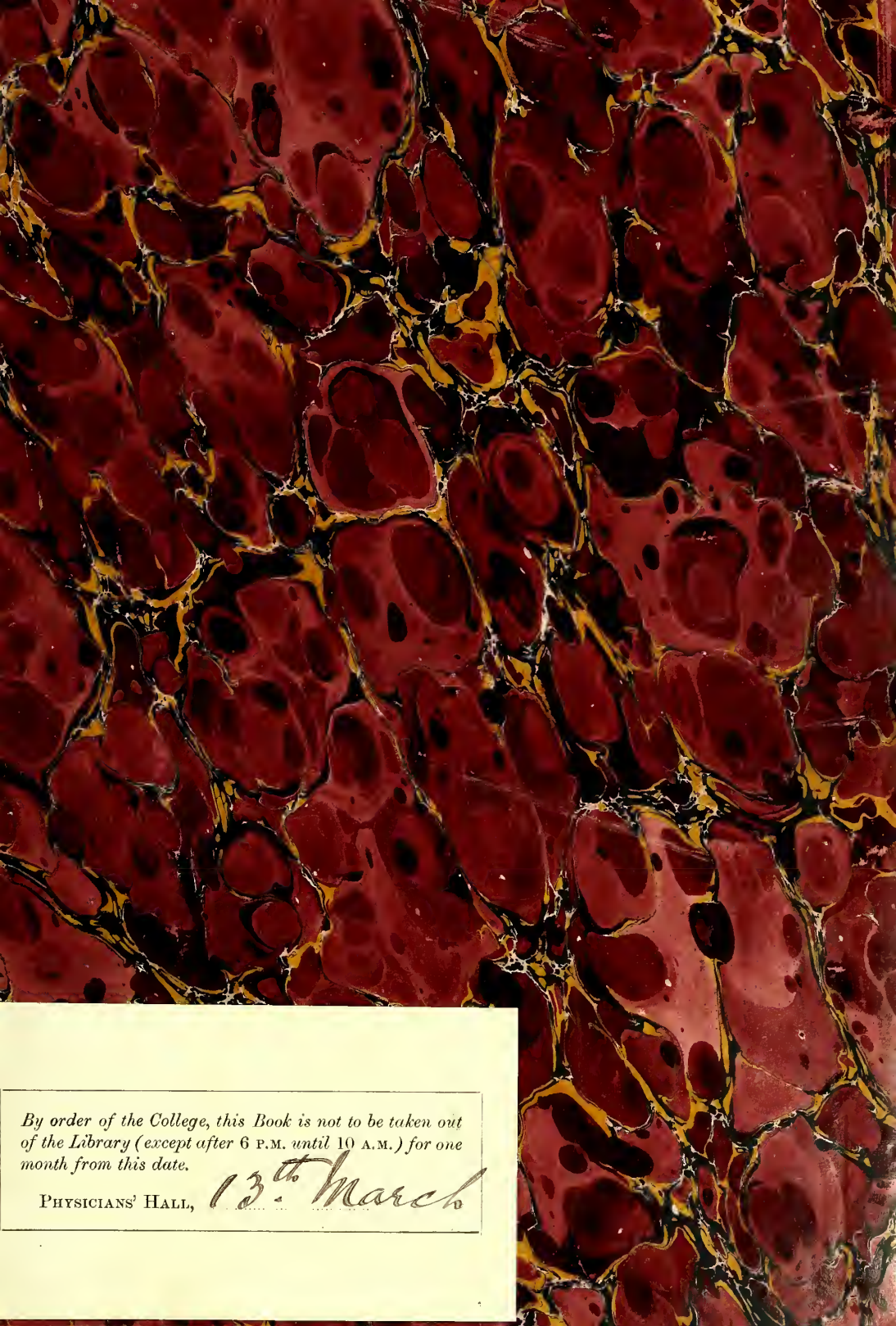


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A DICTIONARY  
OF  
APPLIED CHEMISTRY

VOL. I.

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A DICTIONARY  
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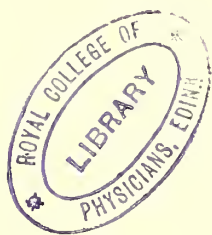
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*ASSISTED BY EMINENT CONTRIBUTORS*

IN THREE VOLUMES

VOL. I.




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# PREFACE

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THIS Work is essentially a Dictionary of Chemistry in its Applications to the Arts and Manufactures; hence it deals but sparingly with the purely scientific aspects of Chemistry, unless these have some direct and immediate bearing upon the business of the technologist. For all such matters reference is made to the New Edition of 'Watts' Dictionary of Chemistry,' by Dr. Forster Morley and Mr. Pattison Muir, to which, indeed, the present Work may be said to be complementary. In order to facilitate such reference the general plan and method of arrangement of the two Dictionaries are similar, and the nomenclature and notation adopted are practically identical. It has, however, not been thought desirable, even if it had been found possible, to make use of the same elaborate system of abbreviation and contracted expression as that employed in the companion Work, in which the variety and complexity of the subject-matter are necessarily much greater.

Although the two Works are, in a broad general sense, complementary, it is practically impossible to avoid a certain amount of overlapping, and therefore a certain degree of independence. Hence in the present Work the chemical history of a product of technical importance, so far as it is known, has often been completed although its derivatives have, at present, no applications in the Arts. Moreover, such subjects as the ATMOSPHERE, WATER, FERMENTATION, the CHEMISTRY OF THE HYDROCARBONS, the VEGETO-ALKALOIDS, GLUCOSIDES, &c. &c., all of which are dealt with in the other Work, find also a place in this Dictionary by reason of their relations to Technology or to Medicine and Sanitation. In all cases, however, these subjects are treated from the standpoint of practical application.

The Editor has been fortunate in securing the co-operation of a large number of gentlemen, not only in the United Kingdom, but also in America, Germany, Switzerland, &c., as contributors on subjects with which they are specially qualified to deal. A list of these, with the titles of their contributions, is prefixed to each volume. Their names and standing are a sufficient guarantee that no pains have been spared to make the Work a faithful record of the present condition of Chemistry in its relations to the Arts and Manufactures. Special attention has been paid to the bibliography of the subjects, and in certain cases to the compilation of trustworthy patent-lists.

The Editor desires to express his acknowledgments to Messrs. F. B. Guthrie, G. T. Holloway, Herbert Ingle, H. A. Lawrance, T. A. Lawson, J. Mills, and W. P. Wynne, for assistance in the compilation of the subject-matter of certain of the articles; and he is under obligations to his colleagues Messrs. Japp, Howes, and Scott for aid in the revision of the proof sheets.

# ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

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<i>A.</i> . . . .	Liebig's Annalen der Chemie.
<i>A. a.</i> . . . .	Annales Agronomiques.
<i>A. Ch.</i> . . . .	Annales de Chimie et de Physique.
<i>P. Am. A.</i> . . . .	Proceedings of the American Academy of Arts and Sciences.
<i>Am.</i> . . . .	American Chemical Journal.
<i>Ann. M.</i> . . . .	Annales des Mines.
<i>Am. S.</i> . . . .	American Journal of Science.
<i>A. C. J.</i> . . . .	Journal of the American Chemical Society.
<i>Am. Ch.</i> . . . .	American Chemist.
<i>Am. J. Pharm.</i> . . . .	American Journal of Pharmacy.
<i>An.</i> . . . .	The Analyst.
<i>Ar. N.</i> . . . .	Archives néerlandaises.
<i>Ar. Ph.</i> . . . .	Archiv der Pharmacie.
<i>B.</i> . . . .	Berichte der deutschen chemischen Gesellschaft.
<i>Bl.</i> . . . .	Bulletin de la Société chimique de Paris.
<i>B. B.</i> . . . .	Berliner Akademie-Berichte.
<i>B. C.</i> . . . .	Biedermann's Centralblatt für Agricultur-Chemie.
<i>B. J.</i> . . . .	Berzelius' Jahresberichte.
<i>B. M.</i> . . . .	Berliner Monatsberichte.
<i>Bentl. a. T.</i> . . . .	Bentley and Trimen. Medicinal Plants.
<i>Bl. Ph.</i> . . . .	Bulletin de Pharmacie.
<i>C. S. Mem.</i> . . . .	Memoirs of the Chemical Society of London.
<i>C. J.</i> . . . .	Journal of the Chemical Society of London.
<i>C. J. Proc.</i> . . . .	Proceedings of the Chemical Society of London.
<i>C. N.</i> . . . .	Chemical News.
<i>C. R.</i> . . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences - Paris.
<i>C. C.</i> . . . .	Chemisches Central-Blatt.
<i>D. P. J.</i> . . . .	Dingler's polytechnisches Journal.
<i>Fl. a. H.</i> . . . .	Flückiger and Hanbury. Pharmacographia 2nd Ed.
<i>Fr.</i> . . . .	Fresenius' Zeitschrift für analytische Chemie.
<i>J.</i> . . . .	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
<i>J. A.</i> . . . .	Jahresbericht der Agricultur-Chemie.
<i>J. C. T.</i> . . . .	Jahresbericht für Chemische Technologie.
<i>J. M.</i> . . . .	Jahrbuch für Mineralogie.
<i>J. Ph.</i> . . . .	Journal de Pharmacie et de Chimie.
<i>J. pr.</i> . . . .	Journal für praktische Chemie.
<i>L. V.</i> . . . .	Landwirthschaftliche Versuchs-Stationen.
<i>M.</i> . . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>M. S.</i> . . . .	Le Moniteur Scientifique.
<i>N. J. P.</i> . . . .	Neuer Jahresbericht der Pharmacie.
<i>N. R. P.</i> . . . .	Neues Repertorium für die Pharmacie.
<i>N. J. T.</i> . . . .	Neues Journal von Trommsdorf.
<i>P. M.</i> . . . .	Philosophical Magazine.
<i>P.</i> . . . .	Poggendorff's Annalen der Physik und Chemie.
<i>Ph.</i> . . . .	Pharmaceutical Journal and Transactions.
<i>Ph. C.</i> . . . .	Pharmaceutisches Central-Blatt.
<i>Ph. Centh.</i> . . . .	Pharmaceutische Central-halle.
<i>Pr.</i> . . . .	Proceedings of the Royal Society.
<i>P. R. I.</i> . . . .	Proceedings of the Royal Institution of Great Britain.
<i>R. P.</i> . . . .	Repertorium für die Pharmacie.
<i>S. C. I.</i> . . . .	Journal of the Society of Chemical Industry.
<i>Sitz. B. or Sitz. W.</i> . . . .	Sitzungsberichte der K. Akademie zu Wien.
<i>Tr.</i> . . . .	Transactions of the Royal Society.
<i>U.</i> . . . .	Ure's Dictionary of Arts, Manufactures and Mines. 7th Ed.
<i>W.</i> . . . .	Wiedemann's Annalen der Physik und Chemie.
<i>W. J.</i> . . . .	Wagner's Jahresbericht.
<i>Z.</i> . . . .	Zeitschrift für Chemie.

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# A DICTIONARY OF APPLIED CHEMISTRY.

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**AAL, A'L, ACH or AÍCH.** Native names for the roots of *Morinda tinctoria* and *M. citrifolia* which are extensively employed in various parts of India, under the general trade name of *Suranji*, as a dye-stuff, more especially for dyeing reds, purples, and chocolates. These plants are to be met with in nearly all the provinces of India, either wild, as in the jungles of Bengal, or cultivated in small patches in betel-nut plantations, or near the homesteads of the dyers.

In Bengal, the plant is usually propagated by slips or cuttings, but in other parts it is raised from seed, as well as from cuttings. When the plants have attained a height of some five or six feet, that is, as a rule, at about the end of the third year, the straight spindle-shaped roots, which extend into the ground to a depth of three or four feet, are dug out, and the upper portions of the plant are cut into slips to serve for the propagation of the next crop.

The colouring matter is found principally in the root-bark, and is developed in greatest quantities at about the end of three or four years, depending upon the character of the soil. After this time, the dyeing matter gradually disappears, and the matured trees, which eventually attain the height of a mango tree, contain hardly a trace of it. The thin roots are the most valuable, roots thicker than half an inch being thrown away as worthless. They are mainly used for dyeing the thread or yarn from which the coloured borders of the cotton garments worn by the lower classes are woven, but they are also occasionally employed for dyeing the coarse cotton fabric called 'Khárua,' or for dyeing the silk thread which forms the border of the silk fabric known as 'Endi' cloth. The colours given by A'l range from a reddish-yellow through pink and various shades of red to a dark brown-red. The tint seems primarily to depend upon the age of the root, and upon the proportion of root-bark to root-stem which is employed. The root-bark gives the best reds; the dye in the woody part of the root is yellow, and hence when the wood preponderates over the bark the

resulting dye is reddish-yellow. The methods of A'l-dyeing differ considerably in various parts of India. The usual plan in Bengal is to steep the cloth or yarn in a mixture of powdered castor-oil seeds and the ashes of plantain leaves or other alkaline ashes and water, for some days with alternate washing and drying, after which it is boiled with the dyeing solution prepared by treating the pounded roots, or sometimes the root-bark only with water.

Myrabolans, turmeric, the bark or leaves of *Symplocos racemosa*, alum, certain gums, and various other substances are occasionally used as mordants or auxiliaries either immediately after the cleansing process or along with the dye-stuff; frequently, however, the cloth is transferred directly from the cleansing liquor to the decoction of the root, and no mordant is employed. Purples and chocolates are obtained by adding sulphate of iron to the dyeing liquor.

The active dyeing principle of A'l seems to be *Morindin*, a crystallisable glucoside first isolated by Anderson, and further investigated by Stein, and Thorpe and Greenall (Anderson, A. 71, 216; Thorpe and Greenall, C. T. 51, 52; Liotard, Indian Dyes; McCann, Dyes and Tans of Bengal) (*v.* MORINDIN and MORINDON).

**ABACA.** A species of fibre obtained from the Philippine Islands, and used in the manufacture of mats, cordage, &c.

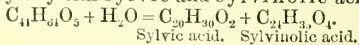
**ABIES.** The spruce-firs: a genus of trees belonging to the Conifers, the most important member of which is the Norway Spruce (*A. excelsa*), constituting the 'White Norway,' Christiania, and Danzig deals of the timber merchant, much used for flooring, joists, and rafters. The waste portions of the trunks and smaller branches are made into splints for the match manufacturer (*v.* MATCHES). Spruce wood is also used in the manufacture of paper (*v.* CELLULOSE). 'Spruce rosin' or 'frankincense' is mainly obtained from *A. excelsa*, and is used in making the better varieties of Burgundy pitch (*v.* BURGUNDY PITCH). The bark and young cones of spruce are employed as tanning materials by the Norse peasantry, and an infusion of the buds in

milk is used by them as a remedy for scurvy. Spruce beer is made by adding a decoction of the green cones to the wort before fermentation. The Black Spruce (*A. nigra*) is chiefly found in Canada and Newfoundland. The spruce beer of America is made from the young shoots of this tree: the concentrated infusion of the buds constitutes 'Essence of Spruce.' Other varieties found in Canada are the White Spruce (*A. alba*), the Hemlock Spruce (*A. canadensis*), the bark of which is used for tanning; and the Douglas Spruce (*A. Douglasii*), which frequently rises to a height of 200 feet with a trunk measuring 8 to 10 in diameter.

**ABIETENE.** A hydrocarbon obtained by distilling the terebinthinate exudation of *Pinus Sabini*, a coniferous tree indigenous to California, and growing on the dry slopes of the foothills of the Sierra Nevada and on the hills along the coast, and known locally as the nut-pine or Digger pine. To procure the exudation, the tree during winter is notched and guttered at a convenient height from the ground, and the resin on distillation yields the liquid hydrocarbon. The crude oil is met with in San Francisco as an article of commerce under the names of 'Abietene,' 'Erasine,' 'Aurantine,' and 'Thioline,' and is used for removing grease-spots, paint-stains, &c., from clothing. It is a nearly colourless mobile liquid of powerful aromatic smell, recalling that of oil of oranges. Its vapour is said to be powerfully anæsthetic, and it has been used with success as an insecticide. It boils at about 100°.

Abietene has been shown by Thorpe to consist almost entirely of *normal heptane*,  $C_7H_{14}$ , mixed with a small quantity of a resin to which its characteristic smell of orange oil is due. (Thorpe, C. J. 35, 296; Schorlemmer and Thorpe, T. 174, 269).

**ABIETIC ACID.** An acid said to exist in colophony, or to be formed from that substance by digestion with dilute alcohol. According to Maly (A. 129, 54; 132, 249) colophony consists chiefly of abietic anhydride  $C_{14}H_{22}O_4$ . By hydration it forms the acid  $C_{14}H_{20}O_5$  which on hydrolysis yields *sylic* and *sylinolic* acids:



According to Strecker (A. 150, 131) and Duvernoy (A. 143, 143) abietic acid is identical with *sylic* acid; v. also Emmerling, B. 12, 1441; Kelbe, B. 13, 888; v. COLOPHONY.

**ABRAUM SALTS.** Ger. *Abraumsalze*: 'Salts to be removed.' The mixed salts found overlying the rock-salt deposit at Stassfurt in Prussia. These consist mainly of rock-salt: *Carnallite*, a double chloride of potassium and magnesium; *Sylvine*, or potassium chloride; and *Kieserite* or magnesium sulphate, v. POTASSIUM.

**ABSINTH.** A liquor flavoured with wormwood (*Artemisia Absinthium*, natural order, *Compositæ*), and other species containing the bitter principle termed *Absinthin*. To prepare absinth, the leaves and flower-heads of the wormwood are steeped in spirit somewhat above 'proof' for several days, with other aromatic herbs—such as angelica root, *Calamus aromaticus*, aniseed, dittany leaves and wild marjoram. The liquid is then distilled, and the green essence thus obtained is mixed with certain aromatic extracts.

A brilliant tint is obtained by the use of in-ligo and other vegetable colouring matters: sulphate of copper is said to have been employed for this purpose; and it is also asserted that the liquor is occasionally adulterated with chloride of antimony in order to produce a characteristic milkiness.

Absinth is largely prepared in Switzerland, especially in the canton of Neuchâtel; and, indeed, the strongest liquor is often known in trade as 'Swiss absinth,' though it may not have been prepared in Switzerland.

**ABSINTHIN** or **ABSANTHIN**  $C_{10}H_{16}O_8$ . The bitter principle of *Artemisia Absinthium*, or wormwood. A yellow crystalline powder, smelling like wormwood: sparingly soluble in water, readily soluble in alcohol and ether (Mein, A. 8, 61; Luck, A. 78, 87; Kromayer, Ar. Ph. [2] 108, 129).

**ABSINTHOL**  $C_{10}H_{16}O$ . The essential principle of oil of wormwood. Isomeric with common camphor, from which it differs by not being converted into camphoric acid by means of nitric acid, nor into campho-carboxylic acid by treatment with carbon dioxide and sodium. With melted potash it gives a resin but no acid. Yields cymene when heated with  $P_2S_5$  and  $ZnCl_2$  (Beilstein and Kupfer, B. 6, 1183; A. 170, 290; Wright, C. T. 27, 1 a. 319).

**ABUTILON INDICUM, PETAREE, or TUBOCUTY.** The bark of this tree consists of long, thin, tough fibrous strips, and, according to Dymock (Ph. [3] 8, 333), is worthy of attention as a source of fibre.

**ABYSSINIAN GOLD.** A yellow alloy of 90-74 parts of copper and 8-33 of zinc. The ingot is plated on one side with a thin plate of gold, and it is then rolled out into sheets, from which articles of jewellery are formed in the usual way: the amount of gold on the finished article varying from 0-03 to 1-03 p.c. Known also as *Talmi gold*. The term is sometimes applied in trade to Aluminium Bronze, v. *Alloys*, art. ALUMINIUM.

**ACACIA CATECHU or KHEIR** (*Mimosa Catechu*, Lin.) is a tree growing in mountainous places in various parts of India. Its unripe pods and wood, by decoction, yield a catechu, known by the name of Cutch or Kutch, which must not be confounded with the official catechu (*Catechu pallidum*). It is used in the preparation of some leathers and by dyers.

**ACACIA GUM or ACACIN** v. GUMS.

**ACAROD RESIN or BOTANY BAY RESIN** v. *Xanthorrhoea Balsans*, art. BALSAMS.

**ACENAPHTHENE**  $C_{12}H_{10}$  i.e.  $C_{10}H_8 \cdot C_2H_2$ . A crystalline substance found in coal-tar oil (Berthelot, Bl. [2] 8, 226). Obtained by cooling the fraction of heavy coal-tar oil which boils between 260°-270°. On re-crystallising the solid product from alcohol, acenaphthene is obtained in long needles, m.p. 95° (Behr and Dorp, A. 172, 265), 103° (Schiff, A. 223, 263); b.p. 278°. For other modes of formation and reactions v. WATTS' DICTIONARY OF CHEMISTRY.

**ACETAL**  $C_2H_5O_2$  or  $CH_3CH(OC_2H_5)_2$  (Döbereiner, Gm. 4, 805; Liebig, A. 5, 25; 14, 156; Stas, A. Ch. [3] 19, 146; Wurtz, A. Ch. [3] 48, 370; Geuther, A. 126, 63).

*Preparation.*—To prepare acetal by Wurtz's method, 2 parts of alcohol are added to a mixture of 3 parts of manganese dioxide, 3 parts of



sulphuric acid and 2 parts of water, and, after the effervescence produced during the first moments of the reaction has subsided, the whole is heated at  $100^{\circ}$  until 3 parts have distilled over. The product is then fractionally distilled, and two portions, one boiling below  $80^{\circ}$  and the second boiling at  $80^{\circ}$ – $95^{\circ}$ , are collected.<sup>1</sup> The former fraction is treated with calcium chloride; the ethereal layer which separates is distilled, and that portion boiling above  $60^{\circ}$  is again treated with calcium chloride to separate the impure acetal; the second fraction  $80^{\circ}$ – $95^{\circ}$  is also rectified, and the ethereal layer obtained on treating the first portion of the distillate with calcium chloride contains acetal and is added to the other. The product so obtained contains aldehyde and ethyl acetate in addition to acetal, and to remove these it is shaken with concentrated aqueous potash, the brown liquid separated from the aqueous layer is distilled, and the distillate shaken with calcium chloride. The ethereal layer is then heated with twice its volume of concentrated aqueous soda in sealed tubes in a water bath for 24 hours, separated from the soda, distilled, the distillate again rectified, and the fraction  $100^{\circ}$ – $105^{\circ}$ , which constitutes the greater portion, is acetal.

In addition to its formation as a by-product in the oxidation of alcohol, acetal can also be obtained from a mixture of acetaldehyde (1 vol.) and absolute alcohol (2 vols.) by heating it with acetic acid ( $\frac{1}{2}$  vol.) for 12 hours at  $100^{\circ}$  (Geuther, A. 126, 63); by cooling it in a freezing mixture, passing dry hydrogen chloride to saturation, and decomposing the resulting monochlorether with sodium ethoxide (Wurtz and Frapollis, C. R. 67, 418; A. 108, 223); or by cooling a mixture of equal volumes to  $-21^{\circ}$ , and passing a current of pure hydrogen phosphide for 24 hours (Engel and Girard, C. R. 92, 692; J. 1880, 694).

**Properties.**—Acetal is a colourless liquid with a peculiar agreeable odour. Its b.p. =  $104^{\circ}$ , and sp. gr. =  $0.821$  at  $22.4^{\circ}$  (Stas, A. 64, 322); b.p. =  $103.7^{\circ}$ – $104.3^{\circ}$  at  $714.4$  mm., and sp. gr. =  $0.8314$  at  $24^{\circ}$  (Brühl, A. 203, 25). It is soluble in 18 vols. of water at  $25^{\circ}$ , and the solubility increases as the temperature rises; from the aqueous solution it is separated as an ethereal layer on addition of concentrated calcium chloride solution (Stas). Acetal is miscible in all proportions with alcohol and ether, does not reduce ammoniacal silver solution, and is unaltered on exposure to air; platinum black, however, oxidises it first to acetaldehyde and subsequently to acetic acid.

**Reaction.**—Acetal does not give the iodoform reaction when added to potassium hydroxide and iodine in aqueous solution, but a separation of iodoform is obtained if it is first shaken with a few drops of hydrochloric acid, owing to the fact that acetal is thereby hydrolysed into a mixture of alcohol and aldehyde.

**Derivatives.**—Mono-, di-, and trihaloacetal are obtained as intermediate products in the preparation of chloral by passing chlorine through 80 per cent. alcohol (Lieben, A. Ch. [3] 52, 313; Paternò, C. R. 67, 765). According to Krey (J. 1876, 475) a better yield of these derivatives is

obtained if a mixture of 2 parts of absolute alcohol, 3 parts of manganese dioxide, 3 parts of sulphuric acid, and 2 parts of water is heated until  $\frac{2}{3}$  of the liquid has distilled over and chlorine is passed through the well-cooled distillate until it shows signs of turbidity. In either case the product is treated with 3–4 vols. of water, the separated oil again washed with water, dried over calcium chloride, and submitted to fractional distillation. The fraction  $80^{\circ}$ – $120^{\circ}$  contains chiefly aldehyde and compound ethers,  $120^{\circ}$ – $170^{\circ}$  chiefly monochloroacetal,  $170^{\circ}$ – $185^{\circ}$  dichloroacetal (Lieben, *l.c.*), and the fraction boiling above  $185^{\circ}$  contains trihaloacetal (Paternò, *l.c.*). These compounds may then be obtained in the pure state by repeated fractionation.

**Monochloroacetal**  $\text{CH}_3\text{Cl}.\text{CH}(\text{OC}_2\text{H}_5)_2$  (Lieben, A. 116, 193; Paternò and Mazzara, B. 6, 1202; Klein, J. 1876, 336; Natterer, M. 3, 444; 5, 497; Wislicenus, A. 192, 106; Frank, A. 206, 341) is a colourless liquid, having an aromatic ethereal odour. Its b.p. =  $156.8^{\circ}$ , and sp. gr. =  $1.0118$  at  $0^{\circ}$ , and =  $1.026$  at  $15^{\circ}$  (Klein). When heated with bleaching powder it yields di- and tri-chloroacetal, chloroform and chlorinated acetaldehyde (Goldberg, J. pr. [2] 24, 107).

**Dichloroacetal**  $\text{CHCl}_2.\text{CH}(\text{OC}_2\text{H}_5)_2$  (Jacobsen, B. 4, 217; Pinner, B. 5, 148; A. 179, 34; Krey, *l.c.*; Paternò, A. 149, 372; 150, 134) boils at  $183^{\circ}$ – $184^{\circ}$ , and has a sp. gr. =  $1.1383$  at  $14^{\circ}$ .

**Trichloroacetal**  $\text{CCl}_3.\text{CH}(\text{OC}_2\text{H}_5)_2$  (Byasson, Bl. 32, 304; Wurtz and Frapollis, J. 1872, 438) boils at  $197^{\circ}$ ; at  $204.8^{\circ}$  at  $753.7$  mm. (Paternò and Pisati, J. 1872, 303), and has a sp. gr. =  $1.2813$ . When heated with concentrated sulphuric acid it yields chloral.

**Trichloroacetal**  $\text{C}_6\text{H}_{11}\text{Cl}_3\text{O}_2$ . Obtained by the action of chlorine on alcohol (Lieben, Paternò, Krey, *l.c.*) crystallises in monoclinic needles resembling caffeine, and melts at  $89^{\circ}$ .

**Monobromoacetal** (Pinner, B. 5, 149; Wislicenus, A. 192, 112).

**ACETALS.** (Wurtz, A. Ch. [3] 48, 370). The acetals are a group of compounds formed by the combination of 1 mol. of an aldehyde with 2 mols. of an alcohol, and the elimination of the elements of 1 mol. of water. They are generally obtained as by-products in the preparation of aldehydes by the oxidation of the corresponding alcohols, the aldehyde at the moment of formation uniting with the alcohol, and this tendency to combine is much increased if acetic acid is present (Geuther, A. 126, 65), or if pure (non-spontaneously inflammable) hydrogen phosphide is passed through the cooled mixture of aldehyde and alcohol (Girard, C. R. 91, 629; J. 1880, 695).

**Properties.**—The acetals are liquids having aromatic odours, and are sparingly soluble in water, from which they can again be separated on addition of concentrated calcium chloride solution. When heated in a closed tube with glacial acetic acid, the corresponding aldehyde is obtained (Beilstein, A. 112, 239). According to Baehmann (A. 218, 45) the series of acetals can be descended by heating any member of the group with an alcohol containing a smaller number of carbon atoms than is present in its alcohol-residue; for example, diethylacetal and methyl alcohol yield dimethylacetal and ethyl alcohol; but the reverse change, if it occurs at all, results

<sup>1</sup> The b.p. is given as in the original paper, but, inasmuch as b.p. of acetal is  $104^{\circ}$ , it seems probable that  $95^{\circ}$  is a misprint for some higher temperature—say  $105^{\circ}$ .

in the production of very small quantities of the higher acetal. Mixed acetals—that is, acetals containing two different alcohol residues—have been described by Bachmann (*l.c.*), but these consist of mixtures of molecular proportions of two distinct acetals (Rübencamp, A. 225, 271).

The following acetals have been prepared: methylal (Kane, A. 19, 175; Brühl, A. 203, 12); ethylidene-dimethyl ether (Arlsberg, J. 1864, 485), -dipropyl, and -diisobutyl ether (Girard, J. 1880, 695), and -diisoamyl ether (Arlsberg, J. 1864, 486); propylenedipropyl ether (Schudel, M. 5, 247); isobutylenediethyl ether (Oeconomidès, Bl. 35, 500); and amylenedi-methyl, -diethyl, and -diisoamyl ether (Arlsberg, *l.c.*). Glycolacetal, a derivative of glycolaldehyde, has also been prepared (Pinner, B. 5, 150).

#### ACETAMIDE $C_2H_5NO$ , or $CH_3CONH_2$ .

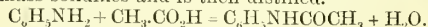
*Preparation.*—(Hofmann, B. 15, 980; Schulze, J. pr. [2] 27, 512; Keller, J. pr. [2] 31, 364). Acetamide is usually prepared by the dry distillation of ammonium acetate; a large quantity of ammonia is evolved at first, but when the temperature rises to  $160^\circ$  an acid distillate, which does not crystallise and consists probably of acid acetate of ammonium, is obtained; above  $160^\circ$  a product containing acetamide distils over and crystallises in the tube of the condenser, whilst above  $190^\circ$  nearly pure acetamide is obtained (Kündig, A. 105, 277).

*Properties.*—Acetamide forms white hexagonal crystals having a peculiar odour, melts at  $82^\circ$ – $83^\circ$  (Hofmann, B. 14, 2729), boils at  $222^\circ$  (cor.) (Kündig), is readily soluble in water, and when heated with acids or alkalis is converted into acetic acid and ammonia. Chlorine, led into fused acetamide, yields acetchloramide  $CH_3CONHCl$ , and bromine, in the presence of dilute aqueous potash or soda, yields acetbromamide, which on distillation with concentrated aqueous soda is converted into methylamine (Hofmann, B. 15, 408). Acetamide acts both as a base and an acid (Pinner and Klein, B. 10, 1896), combining with hydrogen chloride and nitric acid, and forming compounds in which a metal takes the place of one atom of hydrogen, as  $C_2H_4O.NHAg$  (Strecker, A. 103, 321). Mono-, di-, and tri-chloroacetamide have also been prepared (Willm, A. 102, 110; Geuther, J. 1864, 317; Pinner and Fuchs, B. 10, 1066; Malaguti, A. 56, 286; Cloëz, A. 60, 261; Bauer, A. 229, 165).

*Diacetamide*  $C_4H_8NO_2$ , or  $NH(C_2H_3O)_2$ , Gautier, Z. 1869, 127; Hofmann, B. 14, 2731).

*Triacetamide*  $C_6H_8NO_3$ , or  $N(C_2H_3O)_3$  (Wichelhaus, B. 3, 817), and derivatives from them, have also been obtained.

**ACETANILIDE**, also known as **ANTIFEBRIN**, is prepared by heating together glacial acetic acid and aniline for some time. The mass solidifies and is then distilled.



The substance melts at  $114^\circ$  and boils without decomposition at  $295^\circ$ , and it is soluble in hot water, alcohol, and ether.

It is decomposed by boiling with alcoholic potash forming aniline and potassic acetate.

**ACETIC ACID.** *Acide Acétique. Essigsture. Acidum Aceticum.*  $C_2H_4O_2$  i.e.  $CH_3COOH$ , or  $C_2H_3OH$ .

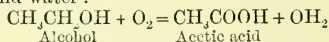
Acetic acid occurs in nature in the juices of

many plants, especially trees, either as free acid or, generally, as the calcium or potassium salt; and, in the form of organic acetates, in the oils from many seeds. It is stated to be present in larger quantities when the plants are kept from the light. It exists in certain animal fluids; Béchamp states it to be a normal constituent of milk. Gmelin and Geiger have found it in mineral waters, doubtless from the decomposition of organic matter.

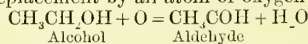
Being a very stable body both at the ordinary and at high temperatures, it is found as a product of the decomposition or destructive distillation of many organic substances. Acetic acid was first shown by Lavoisier to be formed by the oxidation of alcohol. Its true composition was ascertained by Berzelius in 1814, and Döbereiner in 1822 proved that it was formed, together with water, by the oxidation of alcohol, without the formation of carbonic acid as had been previously supposed.

*Preparation.*—Acetic acid is produced by the oxidation, decomposition, and destructive distillation of many organic bodies. The greater part of that used in commerce is produced in the destructive distillation of wood.

By the action of oxygen on alcoholic liquids under the influence of ferments, vinegar is produced, of which the active constituent is acetic acid. Alcohol may be converted into acetic acid by powerful oxidising agents, such as chromic acid, nitric acid, &c. Advantage may be taken of the fact that spongy platinum or platinum black has the property of absorbing oxygen, and thus acting as a powerful oxidising agent. If a tray of spongy platinum be placed over a vessel of alcohol with free access of air, the platinum absorbs at the same time the oxygen and the alcohol vapour, which, being brought into such immediate contact, combine and produce acetic acid and water:—



In addition to the acetic acid, aldehyde (acetic aldehyde) is produced, which is intermediate in composition between alcohol and acetic acid. It is formed by the removal of two atoms of hydrogen from the alcohol without their replacement by an atom of oxygen:—



In presence of excess of oxygen aldehyde forms acetic acid. Aldehyde is a very volatile liquid, and is liable to be lost before its conversion into acetic acid; it is therefore necessary in all cases where acetic acid is produced by the oxidation of alcohol to allow free access of air.

This method produces a very pure acetic acid, but on account of the initial cost of the platinum (which, however, is not in any way injured by use) it is not used on the manufacturing scale. An apparatus has been made in Germany which contained a large number of small vessels, each surmounted by a watch-glass containing platinum black. The temperature was kept at  $33^\circ C$ ., and a constant current of air passed through, the products, as they passed out, being conveyed through condensers so that all the acid was saved. The apparatus, of 40 cubic metres capacity, contained 17 kilos of

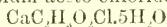
platinum, and converted 150 litres (33 gallons) of alcohol into pure acetic acid daily.

The action of the atmospheric oxygen may, however, be assisted in other ways. The ferment known as the 'vinegar plant,' 'mother of vinegar,' *Mycoderma vini*, or *Mycoderma aceti*, has this power, and appears, like platinum, to absorb the oxygen and oxidise the alcohol within its pores. It is a white gelatinous nitrogenous plant, requiring for its healthy growth albuminous substances and mineral salts, which are always present in wines and other alcoholic liquids. On account of the absence of this food it has no action on pure alcohol, but Pasteur has shown that pure alcohol, to which alkaline phosphate and ammonium phosphate have been added, is slowly aceticated by this ferment, the ammonia, instead of the albuminous substances, supplying the nitrogen.

The *concentrated* or *glacial* acid is usually prepared by the distillation of a dry acetate with an equivalent quantity of strong sulphuric acid, or acid potassium or sodium sulphate. The following proportions may be used:—Sodium acetate, 82 parts, or potassium acetate, 98, or calcium acetate, 79, or lead acetate, 163, heated with 49 concentrated sulphuric acid, or 136 acid potassium sulphate.

Sodium acetate being easily obtainable is generally used. It is first rendered anhydrous, and then fused in sheet-iron pans, 6 feet by 4 feet, care being taken that no sparks reach the dried salt, as it would then ignite and burn like tinder. The mass is cooled, broken into small lumps, and distilled with concentrated sulphuric acid. The distillate contains a small quantity of water, and is redistilled. The first portion distilling contains the water, the later portion is collected and cooled; when crystals of the glacial acid have formed the still liquid portion is removed, the crystals are melted and redistilled as before, producing the glacial acid.

When a solution of calcium chloride is mixed in proper proportions with a solution of calcium acetate, fine large crystals of a double compound, calcium aceto-chloride



gradually separate. H. B. Condé has found that these crystals may be produced in comparative purity even when impure *brown* acetate of lime is used, and has patented (1858) a process for the preparation of pure acetic acid by means of this salt. The ordinary commercial or 'distilled' acetate of lime is generally used. It is mixed with the proper proportion of calcium chloride, and the solution is concentrated by evaporation until crystallisation has commenced, and is cooled; the mother-liquor is poured from the crystals and concentrated with the production of a second crop of crystals; this is repeated until about four crops have been produced. The crystals are then dissolved in water, filtered through animal charcoal, mixed with about 10 p.c. of calcium chloride, and recrystallised. The crystals are distilled with a mixture of 1 part sulphuric acid of sp.gr. 1.84 and 2 parts water, and the acetic acid concentrated in the usual way. Very pure acid is manufactured by this process. The glacial acid may also be prepared by the dis-

tillation of di- or acid-acetate of potash, which, when heated, decomposes into acetic acid and the normal acetate of potash. If ordinary acetic acid be heated with normal potassium acetate, the acid acetate is formed, and a weaker acid at first distils over; as the temperature rises, the diacetate commences to decompose, and the distillate increases in strength until the glacial acid passes over. When the temperature reaches 300°C. the distillate becomes coloured from the decomposition of the acid (Melsens, A. 52, 274; C. R. 19, 611).

By repeated fractional distillation of a weak acid the glacial acid, which boils at the higher temperature, may be produced.

T. Goring (D. P. J. 254, 90-91) advises the addition to dilute acetic acid of substances which combine with the acid but are not soluble in water; the layer of the substance will thus separate the acetic acid from the water, and can itself be removed from the acid by fractional distillation or other means. The method has been patented (Germ. pat. 28064, 1883).

'Aromatic vinegar' is frequently prepared by distilling crystallised diacetate of copper (distilled verdigris). The acetate is dried at 160°C. and distilled in earthenware retorts; the glacial acid distils over, soon becoming coloured green from the presence of copperacetate. It requires to be redistilled. The verdigris produces about half its weight of the acid. The pleasant odour of aromatic vinegar is largely due to the presence of acetone, which is always produced when acetates of heavy metals are distilled, but camphor and essential oils are frequently added to increase or modify the smell.

Pure acetic acid for pharmaceutical and other purposes should not decolourise a solution of permanganate of potash. To remove the organic matter which would have that effect, the acid is distilled with permanganate or dichromate of potash in a copper retort having a silver condenser. The operation is best conducted in an atmosphere of carbonic anhydride to prevent action of the acid on the metals. For *Pyro-ligneous Acid* v. WOOD, DESTRUCTIVE DISTILLATION OF.

*Properties.*—The strongest acid solidifies at 16.7°C. in tabular or prismatic glistening crystals. According to Regnault the glacial acid may be cooled to -10° without solidification, even when agitated, but on the addition of a crystal of the acid the whole solidifies and the temperature rises to 16.7°, the ordinary solidifying point.

The specific gravity of the crystals at 15°C. is 1.0607 (Mendeleef, J. 18.30, 7). They melt to a mobile colourless liquid of sp.gr. 1.0513 at 16.7° (Pettersen, J. pr. (2) 24, 391), 1.0415 at 24° (Brühl), which boils at 118.5°C. at 760 mm. (Perkin). The liquid is unflammable, but the vapour burns with a fine blue flame producing water and carbonic acid. When passed through a red hot tube only a small portion is decomposed producing carbon, acetone, benzene, &c. The strong acid blackens when heated with concentrated sulphuric acid evolving sulphurous and carbonic anhydrides.

Nitric and chromic acids have no action; for this reason acetic acid is frequently used as a solvent for organic substances such as hydro-



carbons, which are to be subjected to the action of chromic acid. Chlorine under the influence of sunlight replaces a portion of the hydrogen, and produces mono-, di-, and trichloroacetic acids. Similarly, bromine produces dibromoacetic acid. On the addition of water to the glacial acid heat is evolved and the density increases until 20 p.c. of water is present; from this strength to 23 p.c. of water the density remains stationary, the amount of water corresponding to a monohydrate  $C_2H_3O_2 \cdot H_2O$ ; Roscoe, however, doubts its existence. Farther dilution lowers the density, so that either dilution or concentration from this point will produce an acid of diminished density.

An acid containing only 43 p.c. of acid has the same density as the glacial acid. This, together

with the slight difference between the density of acetic acid and water, renders it impossible to determine, with any precision, the percentage of acid by means of the hydrometer.

Mohr has determined the densities of mixtures of varying proportions of acetic acid and water, and the percentages of the B.P. are calculated on his results. Oudemans has repeated the determinations at the same temperature ( $15^\circ C.$ ), with different results. According to him the acid used by Mohr contained 5 p.c. water; but, on the other hand, Allen (An. III. 268) has pointed out inconsistencies in the part of Oudemans' table referring to dilute acids. Oudemans' table is, however, generally employed.

The following table shows the density of aqueous acetic acid at  $15^\circ$  and  $20^\circ$ :—

DENSITY OF AQUEOUS ACETIC ACID (OUDEMANS).

p.c.	Density		p.c.	Density		p.c.	Density	
	$15^\circ$	$20^\circ$		$15^\circ$	$20^\circ$		$15^\circ$	$20^\circ$
0	0.9992	0.9983	34	1.0459	1.0426	68	1.0725	1.0679
1	1.0007	0.9997	35	1.0470	1.0437	69	1.0729	1.0683
2	1.0022	1.0012	36	1.0481	1.0448	70	1.0733	1.0686
3	1.0037	1.0026	37	1.0492	1.0458	71	1.0737	1.0689
4	1.0052	1.0041	38	1.0502	1.0468	72	1.0740	1.0691
5	1.0067	1.0055	39	1.0513	1.0478	73	1.0742	1.0693
6	1.0083	1.0069	40	1.0523	1.0488	74	1.0744	1.0695
7	1.0098	1.0084	41	1.0533	1.0498	75	1.0746	1.0697
8	1.0113	1.0098	42	1.0543	1.0507	76	1.0747	1.0699
9	1.0127	1.0112	43	1.0552	1.0516	77	1.0748	1.0700
10	1.0142	1.0126	44	1.0562	1.0525	78	1.0748	1.0700
11	1.0157	1.0140	45	1.0571	1.0534	79	1.0748	1.0700
12	1.0171	1.0154	46	1.0580	1.0543	80	1.0748	1.0699
13	1.0185	1.0168	47	1.0589	1.0551	81	1.0747	1.0698
14	1.0200	1.0181	48	1.0598	1.0559	82	1.0746	1.0696
15	1.0214	1.0195	49	1.0607	1.0567	83	1.0744	1.0694
16	1.0228	1.0208	50	1.0615	1.0575	84	1.0742	1.0691
17	1.0242	1.0222	51	1.0623	1.0583	85	1.0739	1.0688
18	1.0256	1.0235	52	1.0631	1.0590	86	1.0736	1.0684
19	1.0270	1.0248	53	1.0638	1.0597	87	1.0731	1.0679
20	1.0284	1.0261	54	1.0646	1.0604	88	1.0726	1.0674
21	1.0298	1.0274	55	1.0653	1.0611	89	1.0720	1.0668
22	1.0311	1.0287	56	1.0660	1.0618	90	1.0713	1.0660
23	1.0324	1.0299	57	1.0666	1.0624	91	1.0705	1.0652
24	1.0337	1.0312	58	1.0673	1.0630	92	1.0696	1.0643
25	1.0350	1.0324	59	1.0679	1.0636	93	1.0686	1.0632
26	1.0363	1.0336	60	1.0385	1.0642	94	1.0674	1.0620
27	1.0375	1.0348	61	1.0691	1.0648	95	1.0660	1.0606
28	1.0388	1.0360	62	1.0697	1.0653	96	1.0644	1.0589
29	1.0400	1.0372	63	1.0702	1.0658	97	1.0625	1.0570
30	1.0412	1.0383	64	1.0707	1.0663	98	1.0604	1.0549
31	1.0424	1.0394	65	1.0712	1.0667	99	1.0580	1.0525
32	1.0436	1.0405	66	1.0717	1.0671	100	1.0553	1.0497
33	1.0447	1.0416	67	1.0721	1.0675			

The addition of a small quantity of water lowers the melting-point of the glacial acid considerably, as shown by the annexed table (p. 7) (Rüdorff, Ph. [3] II. 241).

Acetic acid is monobasic but forms both acid and basic, as well as normal salts. It dissolves certain metallic oxides, as those of lead and copper, forming basic acetates.

It has a pungent sour taste, is an acrid poison, and when strong blisters the skin. The glacial acid has no action on litmus, but on addition of

water becomes powerfully acid. It is not affected by the electric current, probably because a bad conductor, but when a little sulphuric acid is added the current decomposes it, producing, according to Renard (A. Ch. [5] 16, 289), carbonic anhydride, carbon monoxide and oxygen. Renard also found formic acid in the remaining solution. Alkaline acetates when electrolysed are decomposed into hydrogen and alkaline hydrate which appear at the negative pole, and ethane and carbon dioxide at the positive pole.



Solidifying point °C	Water to 100 parts real acetic acid	Solidifying point °C	Water to 100 parts real acetic acid
+16.70	0.0	+6.25	8.0
16.65	0.5	5.30	9.0
14.80	1.0	4.30	10.0
14.00	1.5	3.60	11.0
13.25	2.0	2.70	12.0
11.95	3.0	-0.20	15.0
10.50	4.0	-2.60	18.0
9.40	5.0	-5.10	21.0
8.20	6.0	-7.40	24.0
7.10	7.0		

Acetic acid mixes with alcohol and ether in all proportions. It dissolves resins, gelatin, fibrin, albumen, essential oils, &c. Phosphorus and sulphur are somewhat soluble in the warm acid. Valenta (D. P. J. 252, 296-297) and others have used it on account of this solvent power in the analysis of oils.

Acetic acid is largely used in the preparation of the acetates of copper, aluminium, iron, lead, &c., as pyrolineous acid in calico printing; in the preparation of varnishes and colouring matters; in the laboratory and certain industries for the solution of hydrocarbons and like substances; for domestic use; in photography; and in medicine as a local irritant and to allay fever, and in the form of smelling salts.

**Analysis.**—Commercial glacial acid should contain at least 97 p.c. of absolute acid. If 9 volumes oil of turpentine be agitated with 1 volume of acid, no turbidity will be produced if the acid contain 97 p.c. or upwards. Acid of 99.5 p.c. produces no turbidity with any proportion of turpentine (Bardy, C. N. 40, 78).

A very delicate test for the presence of water is to mix the acid with an equal bulk of bisulphide of carbon in a dry tube, and warm with the hand for a few minutes; in presence of a trace of water the liquid becomes turbid.

The commercial acid is liable to contain sulphuric acid, sulphates, sulphurous acid, hydrochloric acid, chlorides, arsenic (derived from sulphuric acid), and copper, lead, zinc, and tin derived from the vessels used in the manufacture.

The presence of sulphuric acid or sulphates is shown by the production of a white precipitate with barium chloride. To the filtered solution bromine or chlorine water is added, producing, if sulphurous acid be present, a further precipitate of barium sulphate. Hydrochloric acid and chlorides are detected and estimated with silver nitrate.

In testing for metals a considerable bulk should be evaporated; if much organic matter be present, the liquid should be evaporated to dryness and ignited, and the residue dissolved in hydrochloric acid, a few drops of hydrochloric acid are added, and a current of sulphuretted hydrogen gas passed through the liquid; a black or brown colouration or precipitate indicates lead or copper. Copper may also be detected in the evaporated liquid by the brown precipitate produced on the addition of ferrocyanide of potash, and estimated by electro-deposition.

To test for zinc, the solution, after the passage of sulphuretted hydrogen, is filtered, nearly neutralised with ammonia, and acetate of soda added, when zinc will be precipitated as white sulphide. For arsenic Reinsch's test may be used.

Small quantities of acetic acid may be recognised by neutralising with caustic potash, adding arsenious oxide, evaporating to dryness, and heating, when the characteristic odour of cacodyl is evolved.

To determine the free acetic acid in a solution it is usual to titrate a weighed quantity with a solution of caustic soda standardised with a solution of acetic acid of known strength, or of hydric potassic tartrate (Stillwell and Gladding).

As indicator litmus may be used, but as it is rendered blue by the normal acetate of soda, it is preferable to use phenol-phthalein, to which that substance is neutral; this is also more delicate, and, where the liquid is coloured, may be considerably diluted without impairing the delicacy of the reaction.

To estimate small percentages of water in acetic acid, the melting-point may be determined and the percentage found by the table before given.

Acetates, when heated alone, usually evolve acetone; heated with sulphuric or phosphoric acid they evolve acetic acid; heated with arsenious acid cacodyl is produced.

The acetic acid in acetates may be determined by distilling about 1 gram (15 grains) of the salt nearly to dryness with 10 c.c. of a 10 p.c. solution of phosphoric acid (free from nitric and other volatile acids); water is added and the distillation repeated to remove the last traces of acetic acid; the distillates are mixed and titrated as above with standard alkali. This method of distillation may also be used for highly coloured solutions of acetic acid where direct titration is inadmissible.

### Preparation of Vinegar.

In all processes for the manufacture of vinegar advantage is taken of the oxidising action of the vinegar fungus already described; the souring of wines and other alcoholic liquids is due to this organism, the germs of which are always present in the air and are deposited, and grow in any suitable medium.

The action is more rapid when the liquid is rich in vegetable matter and poor in alcohol, and when the surface exposed to the air is large. The percentage of alcohol should not, however, be too low; the acetous fermentation proceeds but slowly in a liquid containing less than 3 p.c. alcohol.

**Wine vinegar.** Fr. *Vinaigre*; Ger. *Weinessig*. In the great wine district of Orleans, wines which have become sour are generally used for the preparation of vinegar. For this purpose full-bodied wines are preferred. If they contain above 10 p.c. alcohol they are usually diluted or mixed with weaker wines, so as to contain about that percentage. The wine, before being fermented, is usually left for some time in contact with beech shavings, on which the lees are deposited, rendering the wine brighter. A certain amount of extractive matter is, however, necessary for the proper growth of the plant, and if the wine be old and the matter deposited, the

fermentation is much retarded. Wine one year old is preferred.

The 'Vinaigrerie' is usually a building of southern aspect; the rooms in which the process is conducted are low-roofed, and the walls are provided with openings for the admission of air, which can be closed when the temperature is not sufficiently high.

A number of casks of well-seasoned oak, bound with iron hoops, each holding from 50 to 100 gallons, are supported on their sides in rows about 18 inches from the floor, one set being frequently placed above another, in which case those nearest the roof are found to work most rapidly. Each cask is bored with two holes in the front end, a larger one, the 'eye,' for the addition of wine or the removal of vinegar, and a small one for the admission of air.

When first used the casks are thoroughly scalded with boiling water to remove extractive matter, one-third filled with boiling strong vinegar, and allowed to stand for eight days; from that time wine is added in charges of about 10 pints every eight days until not more than two-thirds full; after a further interval of 14 days a portion of the wine, varying from 10 gallons to half the total bulk, is drawn off and the periodical addition of the wine continued. The temperature of the chambers should be about 25°C. and is kept up when necessary with a stove. The workman, in order to ascertain if the fermentation is completed at the end of the usual time, plunges a white spatula into the liquid; if a reddish froth adheres, more wine is added and the temperature raised; a white froth indicates the completion of the process. More than eight days is sometimes required to complete the oxidation, in which case stronger wine and a higher temperature may be used. The sluggishness may, however, be due to the casks becoming foul, which occurs usually after about 6 years' working. The deposit of argol, yeast sediment, &c., is thoroughly removed, the casks cleansed and recharged with hot vinegar as in the case of new casks. Good casks will often last twenty-five years.

When working satisfactorily each cask will produce about twice its capacity of vinegar annually.

Before storing, the vinegar is usually passed through the 'rapes' where it is 'brightened' and the acetification completed.

In other parts of France and in Holland and on the Rhine the following method is used. The wine is placed in two large upright tuns about 9 feet high and 4 feet wide, open to the air. Each tun has a perforated false bottom about 12 inches above the true bottom; on this is placed a quantity of vine cuttings, stalks, &c., so as to expose a large surface for the formation of the fungus. One of the vats is half, and the other completely, filled. The acetification progresses more rapidly in the former; this, after twenty-four hours, is filled from the full cask, in which then the action increases. This alternate transference is continued daily until the acetification is complete. The most favourable temperature is about 21°C. The vinegar is run off into casks containing chips of birch wood on which the lees settle, and in about fourteen days being thus clarified is stored in close casks for the market.

**Malt vinegar.** *Malzgetreide Bieressig. Acetum Britannicum.*—This is prepared from an infusion of malt which has first been fermented to produce alcohol. Six bushels of crushed malt are extracted three times with water, in a circular mash tun supplied with a central stirrer, the first extraction with water at 72°C., the second at a higher temperature, and the third with boiling water. The extracts, which together should not exceed 100 gallons, are passed into a large cast-iron tank 24 feet by 8 feet, cooled by refrigerators to 24°C., poured into a large circular vessel, mixed with 3 or 4 gallons of good yeast and fermented briskly for about forty hours. The extract is filtered, and, where intended for the manufacture of the best keeping vinegar, is stored in casks for some months, whereby the extractive matters which would induce putrefaction are deposited.

This 'wash' may be treated by the 'quick vinegar process' or acetified in large casks lying on their sides in a room at a temperature of about 24°C. The bung-holes of the casks are open, and at each end near the top an opening is made for the circulation of air. When conducted in the open air the process is known as 'fielding'; from eight to twenty rows of casks constitute a vinegar field. The operation is commenced in the spring and completed in about three months in the warmer months.

The fermenting casks are frequently worked in pairs; one being completely and the other three parts filled, acetification progresses more rapidly in the latter; every day a portion is transferred thereto from the full cask, being replaced by an equal amount of the more fermented liquid, until completed.

Before storing, it is necessary to filter the vinegar from the extractive matter. The filtering vessel 'rape' or 'fining tun' is a large cask, usually wider at the base than at the top, fitted with a false bottom, above which it is filled with spent tanner's wood, wood shavings, or, which is far preferable, with 'rapes,' the pressed cake of residue from the British wine manufacture, consisting of the stalks and skins of grapes and raisins. Through this the vinegar is poured, escaping through a tap beneath the false bottom into a tank from which it is continuously pumped to the top of the vessel and again passed through until the last traces of alcohol have been oxidised and the vinegar cleared and brightened. In this way pickling vinegar is produced.

For household vinegar, the malt is acetified in upright casks fitted with false perforated bottoms covered with a layer of rapes; after twenty-four hours it is transferred to another similar cask, remaining there for two or three days, and thence to a third and fourth cask. A portion of the liquid is transferred to the mothers and the remainder allowed to ferment. A little argol is frequently added to produce a flavour of wine vinegar and the liquid clarified with isinglass.

Vinegar casks are made in three sizes, holding 25, 50, and 116 gallons.

**Quick Vinegar Process.** *Schnellessigbereitung.*

This method, which is applicable to any alcoholic liquid, is founded on that proposed in

1720 by Boerhaave, and was first introduced by Schutzenbach in 1823. It differs from the other processes in causing the liquid to expose a very large surface to the action of the air, one gallon being sometimes made to expose a surface of 100 square yards.

The vat is usually from 6 to 12 feet high, and from 3 to 4 feet wide. In England it is frequently as much as 13 feet high, 14 feet wide at the top, and 15 feet wide at the base. At a distance of 18 inches from the bottom, six or more air holes are bored 1 inch in diameter, inclining downwards towards the inside; just above these a false perforated bottom is fixed. A quantity of beechwood shavings is thoroughly washed with hot water, dried and placed on the false bottom, nearly filling the vat. The shavings may be substituted with advantage by pieces of charcoal about the size of a walnut from which the saline particles have been removed by acid and subsequent washing. The acetylising action is assisted by the power of absorbing oxygen possessed by the charcoal.

Near the top of the tun is fixed a wooden disc perforated by holes as large as a quill, about 1 inch apart; through these, twists of cotton yarn or string are passed, of sufficient length to touch the shavings: they are tied into knots at the upper end to prevent them from slipping through. There are also five or six larger holes through which pass glass draught tubes projecting on either side of the disc, 1 to 2½ inches wide and 4 to 6 inches long, firmly fastened so that no liquid can pass round them through the holes.

About 1 inch from the true bottom is fixed a bent tube attached to a tap through which the vinegar is drawn as soon as it rises to a height of about 15 inches. The vessel is closed with a tightly-fitting lid through which a circular opening is cut for the admission of liquid and for the escape of air.

Before commencing the fermentation it is necessary to 'sour' the shavings; for this purpose hot vinegar is poured in from the top and allowed to soak for at least twenty-four hours.

The composition of the fluid used varies considerably: any alcoholic liquid may be used, but the presence of a trace of tarry matter, such as pyroligneous acid, prevents the action. According to Wagner (Chem. Technology) the following mixture is generally used:—4½ gals. (20 litres), brandy of 30° Tralles (12.5 p.c. by weight), 9 gals. vinegar and 27 gals. water, to which is added a mixture of bran and rye to promote the growth of the vinegar fungus.

Another standard liquor is 50 gals. brandy or whisky 52 p.c. by weight, 37 gals. beer or malt wort with about  $\frac{1}{100}$  part of ferment; this is mixed with 3 to 4 volumes of soft water before passing through the tuns. Molasses or honey in the proportion of 2 lbs. to 50 gals. is sometimes added, to produce a more finely coloured vinegar.

For 'wine malt' 40 lbs. wheat-meal and 80 lbs. barley-meal are ground, and mixed together with 40 gals. warm water (50°C.); after settling, the clear liquid is drawn off, the residues are treated with hotter water (70°C.), settled, the liquid removed and the residue again treated, this time with boiling or nearly boiling water, in such quantity that the total washings amount to

about 100 gals. The solution is cooled, mixed with 15 lbs. yeast, and allowed to ferment at 27°C. for five or six days; it is then known as the 'gyle.' The temperature of the chamber being about 38°C. the liquid which, where the 'generator' or 'graduator' is new, is heated to 50°C., or, where in use for some time and thus in good condition, to 25°C., is poured over the upper disc and trickles slowly down the twisted threads, which swell and prevent too rapid passage. As the liquid flows over the shavings it becomes oxidised, the action being more rapid when, after some time in use, the shavings have become coated with the 'mother of vinegar.' When the action is satisfactory the temperature of the interior rises on account of the oxidation to 37°C. and creates a constant upward current of air which passes from the openings below the false bottom, round the shavings and through the tubes in the upper disc.

When the liquid contains no more than 4 p.c. alcohol, the vinegar which collects is entirely aceticified, but where a stronger liquid is used it may be necessary to pass it three or four times through the graduator. When a strong vinegar is required, that produced from one of the above-mentioned liquids is mixed with a more alcoholic liquid, and again passed through, and this may be repeated until 1 oz. of the liquid will neutralise sixty grains pure dry potassium carbonate, corresponding to about 12 p.c. acetic acid by weight. Each graduator will contain about 80 gals. of liquid and will produce daily 15 gals. of good vinegar. One workman usually attends to 10 tuns.

By this process, on account of the large surface exposed, a considerable loss of alcohol, and hence of acetic acid, is unavoidable, amounting when properly carried out to about 6 p.c. of the whole; but if the temperature has been allowed to rise too high, the loss is greatly increased. At the same time sufficient air must be introduced to convert the alcohol directly into acetic acid, or the loss will be further increased by the formation of the volatile aldehyde.

By some makers the vapours from the tuns are passed over or through water to absorb the alcohol and aldehyde. For this purpose two floating gasometers are sometimes used: one rises and removes the air which has performed its work, while the other falls, keeping up a constant current of air through the generator. As each gas-holder falls it discharges the air through a cistern of water, which absorbs the volatile products and is used for the preparation of a further quantity of malt extract.

About one-third of the total extractive matter in the malt is lost or dissipated in the fermentation and aceticification (Ure).

In Singer's generator (*v. C. T.* 1868, 580), a number of vessels are placed one above another in a shed in which a suitable temperature is maintained and from which draughts are excluded. The vessels are connected together by wooden tubes provided with longitudinal slits through which air can pass. The liquid slowly drops through the tubes from one vessel to another, and exposing a large surface: to the air becomes aceticified. It is stated that the loss of alcohol usually experienced is avoided in this process. In many vinegar works the larvae of



the 'vinegar fly' (*Drosophila cellaris*) and 'vinegar eels' (*Anguillula aceti*) abound.

Vinegar is found to be very liable to decomposition when exposed to motion or vibration, probably on account of the lees becoming mixed with the liquid.

In addition to wine and malt, vinegar is prepared from many other substances. Cider vinegar is of a yellowish colour, sp.gr. 1.013 to 1.015. It contains  $3\frac{1}{2}$  to 6 p.c. acetic acid, and on evaporation leaves a mucilaginous residue, smelling and tasting of baked apples, and containing malic acid, but not tartaric acid. The residue varies from 1.5 to 1.8 p.c. Perry and crab apple vinegars are used in Wales and Monmouthshire, and possess characteristic properties.

Ale vinegar is prepared from strong sour pale ale. It usually gives a large residue (5 to 6 p.c.), and is very liable to putrefaction. Crystal vinegar is ordinary vinegar decolourised by filtration through animal charcoal. A household vinegar is prepared in Germany from  $7\frac{1}{2}$  gals. soft water, 2 lbs. honey or brown sugar, 1 gal. whiskey or corn spirit, 2 ozs. cream of tartar.

Glucose or Sugar vinegar is prepared by the conversion of amylaceous substances into sugar, by the action of dilute acids, followed by fermentation and acetification. It is stated to be used for adulterating wine vinegar. It can be distinguished from other vinegars by the addition of 3 or 4 volumes strong alcohol, which produces a slimy precipitate of dextrin. Barium chloride usually gives a copious precipitate, due to the sulphuric acid used in the manufacture of the glucose.

An artificial vinegar is made by mixing acetic acid with water and adding burnt sugar (caramel) and acetic ether to produce the proper colour, odour, and taste. This vinegar differs from genuine kinds by the absence in the evaporated residue of phosphoric, tartaric, or malic acid.

**Properties.**—Malt vinegar is a brown liquid of pleasant refreshing odour. The odour is due to the presence, in addition to the acetic acid, of acetic and other ethers. Acetic ether is frequently added in small quantity to increase this aroma.

The vinegar of the B.P. has a sp.gr. of 1.017 to 1.019. In commerce it usually occurs in four strengths, numbered 18, 20, 22, and 24. The last is 'proof' vinegar, it contains 6 p.c. acetic acid, and its sp.gr. is 1.019. The numbers depend on the fact that one fluid ounce of the liquid will neutralise 18, 20, 22, and 24 grains respectively of pure dry sodium carbonate. The real weight of acetic acid in one ounce of liquid may be found by multiplying its number by 1.132, and the percentage by weight by multiplying the number by 0.259. Thus No. 24 should contain 6.22 p.c. of absolute acetic acid.

The addition of 1 part sulphuric acid to 1,000 parts vinegar is lawful, and is generally made, though the idea that its presence prevents putrefaction has been shown to be erroneous.

Malt vinegar usually contains alcohol, gum, sugar, and extractive matter, acetates, chlorides, free and combined sulphuric acid, and on evaporation and ignition leaves a residue containing much phosphate.

Wine vinegar varies in colour from pale yellow to red; that made from white wine is most esteemed; it usually has an alcoholic odour. Its sp.gr. is 1.014 to 1.022; it contains from 6 to 12 p.c. acetic acid. A litre (1.76 pints) of Orleans vinegar usually saturates 6 or 7 grams (92 to 108 grains) of pure dry sodium carbonate. On evaporation the total extract varies from 1.7 to 2.4 p.c., of which 0.25 p.c. is usually potassium tartrate, a salt peculiar to wine vinegar. The residue, with the exception of the tartar, should dissolve in alcohol.

The proof-vinegars of various countries differ considerably; the minimum of acetic acid allowed by the various Pharmacopœias is—France, 8 to 9 p.c.; England, Germany, and Austria, 6 p.c.; Belgium, 5.6 p.c.; Russia, 5 p.c.; United States, 4.6 p.c. Thus, genuine vinegar seldom falls below 5 p.c., and should be condemned as adulterated with water when the amount is as low as 3 p.c.

The German Pharmacopœia allows an extract of 1.5 p.c., but it has been proposed by the German Pharmaceutical Commission to reduce this to 0.5 p.c. (Ar. Ph. 23, 466).

#### Analysis of Vinegar.

The adulterants to be looked for in vinegar are mineral acids, especially sulphuric acid, more rarely hydrochloric, and still more rarely nitric acid, tartaric acid, and pyroligneous acid; flavouring agents, cayenne, ginger, &c.; impurities—usually derived from the vessels used—copper, lead, zinc, tin, arsenic (from sulphuric acid).

The presence of free mineral acids may be demonstrated by the addition of Paris violet (methylaniline violet). Prepare a solution of this dye by dissolving 1 part in 1,000 parts water, and add two or three drops of the solution to about one ounce of the vinegar. In presence of 1 p.c. free mineral acid the colour is green, with 0.5 p.c. bluish-green, and with 0.2 p.c. blue (Hilger, Ar. Ph. 1876, 193).

If mineral acids are added to vinegar in small quantity they liberate an equivalent quantity of acetic acid from the acetates, until the acetates are wholly decomposed, and form salts with the base, thus ceasing to exist as free acids. As acetates on ignition produce carbonates, the presence of an alkaline reaction in the ash indicates the presence of acetates in the vinegar, and therefore the absence of free mineral acids, though these may have been added in small quantities in the first instance. If, however, the ash be neutral the presence of mineral acids is indicated. Hydrochloric acid may be tested for by adding silver nitrate to the distillate from the vinegar.

Heavy metals may be considered absent if no darkening is produced on passing sulphuretted hydrogen for some time through the solution. To determine the acetic acid in vinegar 110 c.c. may be distilled until 100 c.c. have passed over. The 100 c.c. will contain four-fifths of the total acid, and may be titrated with standard alkali and phenol phthalein, making an allowance for the one-fifth left in the retort.

Cayenne pepper, ginger, and other flavouring matters may be discovered by neutralising the vinegar and tasting.



Chevallier has found fuchsine in French wine vinegars.

#### METALLIC ACETATES.

##### Aluminium acetates.

The triacetate or normal acetate  $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$  is not known. A solution corresponding to this compound, but which appears to be a mixture of the diacetate and acetic acid, is the only acetate of commercial importance. It is known as 'red liquor' or 'mordant rouge,' and is prepared by several methods.

A solution of alum is added to acetate of lime liquor. The lime is precipitated as sulphate, its place being taken by the aluminium forming aluminium acetate; sulphate of ammonia or potash (according to whether ammonia or potash alum has been used) is produced at the same time. The mixture is agitated and allowed to settle, and a small quantity of the clear fluid removed and tested by the addition of alum; if a precipitate forms sufficient alum has not been used and more must be added. The solution is filtered and concentrated to a specific gravity of 1.087 to 1.10 and allowed to deposit the small excess of sulphate of lime, which is still present. Sulphate of lime, being slightly soluble in water, is contained in the liquid in small quantity, and as the colours produced are diminished in brilliancy by the presence of this substance, its value is much reduced. By the substitution of lead acetate for the calcium acetate a much finer product is obtained. For this purpose 100 lbs. alum is dissolved in 50 gallons water, and treated with 100 lbs. finely powdered lead acetate with constant stirring; or, using the same quantities, 10 lbs. crystallised carbonate of soda is added before the acetate of lead; or, to 100 lbs. alum in 50 gallons water 6 lbs. of carbonate are added in small portions followed by 50 lbs. of lead acetate. The addition of the carbonate is made with a view to the production of a basic sulphate of alumina as well as the acetate, and as the sulphate assists the mordanting, less acetate is required. The solutions are allowed to settle and decanted. They contain the aluminium acetate mixed with basic aluminium sulphate and alkaline sulphate.

An aluminium sulpho-acetate appears to act satisfactorily. It is prepared by mixing (1) 453 lbs. ammonia alum (or 383 lbs. aluminium sulphate), 379 lbs. lead acetate, 1,132 lbs. water; or (2) 453 lbs. alum (or 333 lbs. aluminium sulphate) and 158 lbs. acetate of lime. The mixture is agitated, settled, and the clear liquid decanted.

By the use of aluminium sulphate, red liquor of the same density contains much more of the active alumina than that prepared with alum. Thus in a sample of the former 1 gallon contained 4 oz. 416 gr. alumina, while the average amount found in three samples prepared from alum was 3 oz. 245 gr. The addition of a little ammonia or other alkali to the red liquor prepared from aluminium sulphate is advantageous for certain colours. Red liquor usually contains from 3 to 5 p.c. alumina ( $\text{Al}_2\text{O}_3$ ) and 6 to 10 p.c. acetic acid; its density varies from 1.085 to 1.120.

It is largely used in dyeing and calico-printing, especially for the production of red colours, madder reds and pinks (whence its name of red

liquor); for the production of dense lakes, and for waterproofing woollen fabrics.

One-fourth of the total quantity of alum used in England is employed in the preparation of 'red liquor.'

##### Ammonium acetate $\text{C}_2\text{H}_3\text{O}_2\text{NH}_4$ .

The crystalline salt is usually prepared by saturating glacial acetic acid with dry ammonia gas. In solution it may be prepared more cheaply by neutralising acetic acid solution with ammonia. On evaporation, a solution of the salt loses ammonia, and leaves the acid acetate or diacetate.

Ordinary solid ammonium acetate always has an odour of acetic acid; it is very soluble in water and alcohol.

Pure ammonium acetate should be entirely volatilised on heating. The commercial salt is liable to contain the same impurities as sodium acetate.

##### Calcium acetate. Diacetate of lime. Pyrolignite of lime. $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

This important salt is prepared by the neutralisation of acetic acid or pyroligneous acid, with lime or chalk.

In the preparation from pyroligneous acid, the crude acid may be used, in which case the acetate of lime is known as *brown acetate*, or the distilled liquor may be employed producing *grey acetate*. The acid is placed in large wooden or iron pans, and powdered chalk or lime added in slight excess; the liquor remains at rest at a warm temperature until settled, and is then syphoned off into the evaporating pans. It is usually evaporated by coils of pipe through which steam passes, in this case the vessels are usually wooden, and lined with lead, but sometimes iron pans are used, the evaporation being conducted over a fire. As the liquid evaporates, tarry impurities rise to the surface, and are removed with a skimmer. As the acetate forms, it is removed and drained in wicker baskets suspended over the pans.

The proper drying of the salt is an important element in the formation of a good product. In large works a drying house is used, which is usually a wind furnace 7 or 8 feet long,  $4\frac{1}{2}$  feet broad. It is first heated from  $75^\circ\text{C}$ . to  $115^\circ$ , and the fire slackened, the salt is then spread over the bottom to the depth of about 2 inches, and when somewhat dry an equal quantity is spread above it, the salt is repeatedly turned, and the heat continued for about 24 hours. When apparently dry, the heat is increased to about  $125^\circ\text{C}$ . and the last traces of moisture driven off. Care must be taken that the heat is not too high, or the salt becomes decomposed. As in the case of sodium acetate, no sparks must touch the mass, or it may burn away like tinder.

The mass thus produced, when prepared from the *brown liquor*, is dark, containing charcoal and decomposed tarry matters; it may be dissolved in 3 parts hot water, filtered through animal charcoal, and again evaporated and crystallised yielding a nearly colourless product.

Pure calcium acetate crystallises in silky needles or prisms containing two molecules of water. At the ordinary temperature the crystals effloresce partially, and at  $100^\circ\text{C}$ . they become anhydrous, forming a white powder of saline taste, very soluble in water.

Calcium acetate is used in the preparation of other acetates, and of acetic acid, and in calico printing. The pure salt is completely soluble in water and proof spirit. The commercial article usually contains 62 to 67 p.c. of real acetate, and 1 to 8 p.c. of matters insoluble in water. The impurities are hydrate, carbonate and sulphate of lime and tarry matters; formate and other salts of lime with fatty acids also occur.

Many methods of assay for this substance are in use, varying considerably in accuracy. Allen has tested them by assaying by each the same sample of acetate, and his results vary in the extreme cases by as much as 10 p.c. (*Commercial Organic Analysis*, i. 399).

The most trustworthy method is to distil with pure phosphoric acid and titrate the distillate as already described under acetic acid. (*See* Stillwell and Gladding, *The Manufacture and Analysis of Calcium Acetate*, A. Ch. 1884, 94-107.)

**Calcium aceto-chloride**  $\text{CaC}_2\text{H}_3\text{O}_2\text{Cl} \cdot 5\text{H}_2\text{O}$  has already been described as used in Condy's process for the preparation of pure acetic acid.

#### Copper acetates.

The normal *acetate of copper* is prepared by dissolving cupric oxide or verdigris in acetic acid, or by the action of copper sulphate on the acetates of lead, calcium, or barium.

It crystallises in prisms, soluble in 13 parts cold and 5 parts hot water, and in 14 parts alcohol. In commerce it usually occurs in bunches of deep-green coloured non-transparent crystals known as 'grappes.'

Acetate of copper is used in the manufacture of pigments; as an oxidising agent in the indigo bath; and, to a slight extent, for the preparation of acetic acid.

**Basic copper acetate.** *Verdigris. Vert-de-gris. Vert de Montpellier. Grünspan.*

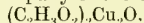
This substance consists of a mixture of mono-, di-, and tri-basic acetates of copper, which are present in different proportions in different varieties of verdigris.

At Grenoble and Montpellier the following process is used: The 'mares' or residues from the wine factories, consisting of the skins and stems of grapes, which were formerly thrown away, are loosely placed in earthen vessels, about 16 feet high, 14 feet in diameter at the widest part, and 12 feet at the mouth, covered and allowed to ferment, until a piece of clear copper (previously moistened with verdigris and dried), on insertion, becomes uniformly coated with green in 24 hours. The fermentation should not proceed too far, or putrefaction is liable to begin.

The copper used is in sheets  $\frac{3}{4}$  inch thick, 4 to 6 inches long, and 3 to 4 broad, each weighing about 4 oz., they are freed from scales, if necessary, rubbed with a solution of verdigris and dried; unless this precaution be adopted, the first coating produced by the mares will be black instead of green. They are heated over a charcoal fire until as hot as the hand can bear, and placed in an earthenware vessel in layers with the mares, the top and bottom layers being composed of the latter material. 30 to 40 lbs. of copper are used for each vessel. In from ten to twenty days, according to the temperature, the covers are removed, when, if the process has progressed favourably, the mares

will be whitish and the copper covered with fine, glossy, green crystals. The plates are then removed and placed on end one against another. After two or three days they are moistened by immersion in water or damaged wine, and again erected for about a week. This alternate moistening and exposure to the air is continued at the same interval for about six or eight weeks. The plates have then become covered with increasing coatings of the verdigris, which is detached and the plates again used until entirely eaten away. The verdigris is kneaded with a little water into leather bags, pressed into rectangular cakes and dried.

This substance is known as blue verdigris, and consists principally of the basic acetate



It should be dry, of a fine bluish colour, and soluble in dilute acids and ammonia.

Green verdigris contains as a principal constituent the basic acetate  $2(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu}_2\text{O}$ , and is prepared by placing the copper plates alternately with cloths moistened every two or three days with pyroligneous acid or acetic acid until the plates show green crystals. The plates are arranged so as to allow free access of air and occasionally moistened, for five or six weeks. Large quantities of verdigris are manufactured in England by this process from pyroligneous acid. The imports of verdigris are very small.

The various forms of verdigris are used as oil and water colours. With white lead it is used in Russia and Holland as an oil paint, which by double decomposition produces a peculiar green. The paint is considered a good preservative. Verdigris is used in dyeing and calico-printing, and for the preparation of Schweinfurth green and other copper paints.

Verdigris is frequently adulterated with chalk, sand, clay, pumice, and sulphates of copper, barium, and calcium. When brass sheets have been used in the preparation instead of copper, zinc will also be present.

When warmed with dilute hydrochloric acid the sand, clay, baryta, &c., will remain undissolved, and may be weighed. The total residue in a good sample will usually amount to 3 p.c., but should not exceed 6 p.c.

**Aceto-arsenite of copper.** *Schweinfurth green (v. ARSENIC).*

**Ferric acetate**  $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$ .

This salt is prepared by the addition of calcium or lead acetate to ferric sulphate or iron alum, avoiding excess of the acetate. It is used as a mordant, its action corresponding to that of aluminium acetate. An alcoholic solution is used in medicine.

For many purposes a mixture of ferrous and ferric acetates is preferred. It is prepared by repeatedly pouring pyroligneous acid on iron turnings until saturated with iron. The liquid is known as 'pyrolignite of iron,' 'bouillon noir,' 'liqueur de ferraille.'

**Ferrous acetate**  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$ . *Pyrolignite of iron; iron liquor or black liquor.* Is prepared on the large scale by the action of crude pyroligneous acid of sp.gr. 1.035 to 1.040 on iron turnings, nails, &c., at a temperature of 55°C. The solution is frequently agitated and the tarry matters skimmed from the surface as they rise.

It is found that the purified acid produces a less satisfactory liquor, a fact due, according to Moyret (J. S. D. C. i. 117), to the presence of a small quantity of pyrocatechol in the crude acid, which forms a compound with the ferrosiferic oxide in the solution, and causes its intense colour and keeping properties.

The liquid is intensely black, of sp.gr. 1.085 to 1.090, and is evaporated until its density rises to 1.120, or sometimes to 1.140. It is then ready for use, and is known as 'printer's iron liquor.' When of density 1.120 the liquor contains about 10 p.c. iron.

The liquor used by dyers is often concentrated, not by evaporation but by the addition of copperas (ferrous sulphate); thus, the addition to 1 gallon of black liquor, sp.gr. 1.085, of  $\frac{1}{2}$  lb. copperas would raise its density to 1.111. Over 1 lb. of copperas has been found in 1 gallon of iron liquor. Tannin also is sometimes added.

Black liquor is also prepared by the action of ferrous sulphate on acetate of lime; the liquor produced has an average density of 1.11, and always contains sulphate of lime. By the action of lead acetate on ferrous carbonate, carbonate of lead and ferrous acetate are produced.

Black liquor absorbs oxygen from the air, forming ferric acetate, which is always present in the liquid. To diminish this action clean metallic iron is frequently added.

It is largely used in calico-printing and in dyeing, in the preparation of blue, violet, black, brown, and other colours, and for producing a black colour on hats, furs, leather, wood, &c.

**Lead acetate.** *Normal or di-acetate of lead. Sugar of lead. Sel de Saturne. Bleizucker.*  $Pb(C_2H_3O_2)_2$ .

For the preparation of *white acetate* of lead, leaden vessels are used, or copper pans, on the bottom of each of which a piece of metallic lead is soldered to produce a galvanic action and prevent the copper from being acted upon. In the vessel acetic acid of 45 p.c. or less is placed, and to 100 parts of 45 p.c., or a proportionate quantity of a weaker acid, 86.5 parts of litharge are added in small quantities, with constant stirring, until the liquid is nearly neutral, it is then heated to boiling and impurities skimmed from the surface, transferred to another vessel and evaporated to a density of 1.5, and removed to the crystallising pans, which are usually of wood, lined with lead or copper, 4 feet by 2 feet, and 6 or 8 inches high. The coarsely crystalline mass thus obtained is drained on wooden racks, and broken into lumps for the market.

A coarser variety, known as *brown acetate*, is prepared by substituting distilled pyroligneous acid for the purer acid. The muddy liquid produced is settled in a large tun, and the supernatant liquid transferred to a large iron pan and heated to boiling. It is again allowed to settle, transferred to another pan, evaporated until crystallisation commences, and about 3 volumes of water added, causing the remaining impurities to rise to the surface. The liquid is skimmed and again evaporated (water being added as before if the liquid is not sufficiently clear) until a small portion of the liquid crystallises, on removing and cooling, to the satisfaction of the workman. It is then ladled into pans and allowed to crystallise.

As a rule, about 3 parts acetate are produced from 2 parts litharge.

By another method granulated lead, white lead residues, &c., are placed in vessels standing obliquely one above another; the upper vessel is filled with strong acetic acid, which after the expiration of half an hour is allowed to run into the second vessel. Every half-hour it is removed to a lower one. The lead, after the acid has been removed, absorbs oxygen rapidly, and becomes heated. After leaving the last vessel, the acid is again passed through, dissolving the acetate which has been formed, and is evaporated and crystallised.

Pure lead acetate is a white crystalline salt of sweetish taste and weak acid reaction, containing 3 molecules of water. It dissolves in 1.5 cold water, and in 0.5 hot water. At 280 C. it melts, and when heated more strongly it forms a basic salt and suddenly solidifies.

Lead acetate is largely used in dyeing and calico-printing, for the preparation of alum mordants, &c., in the manufacture of chrome yellow and other pigments, and in medicine.

Lead forms two well-defined basic acetates—the dibasic acetate  $Pb_2A_2.PbO.aq$  (Wittstein, A. 52, 253), formed by dissolving litharge in the normal acetate in calculated proportions; and the tribasic acetate,  $Pb_3A_2.2PbO.aq$ , prepared by boiling the normal acetate with excess of litharge for some time. Solutions of subacetate of lead are used in medicine as *Gouldard water* and *Liquor plumbi subacetatis*.

#### Magnesium acetate.

A basic acetate of magnesia, prepared by warming the normal acetate with magnesia, is stated to be a powerful antiseptic, disinfectant, and deodoriser (W. Kubel, B. 15, 684-686). A thick syrupy liquid containing suspended magnesium hydrate is said to be used in commerce under the name of 'Sinodor.'

**Potassium acetate**  $C_2H_3O_2.K$  occurs in the sap of many plants, and of trees.

Its mode of preparation is similar to that of sodium acetate. It is a deliquescent crystalline solid soluble in 0.53 parts ice-cold water, and in hot water forms a solution which, boiling at 169°C., contains 80 p.c. of the salt.

When chlorine gas is passed through a solution of acetate of potash, carbonic acid is evolved and a very powerful, unstable, bleaching fluid is produced.

Potassium acetate is liable to contain the same impurities as the sodium salt. The di- and tri-acetates are prepared like those of sodium.

**Sodium acetate**  $C_2H_3O_2.Na$  is formed (1) by the action of dilute acetic acid on sodium carbonate, the solution being evaporated and crystallised; (2) by neutralisation of pyroligneous acid with soda, and evaporation and fusion of the salt to remove tarry matters; (3) by the addition of Glauber's salt to solution of acetate of lime or of lead. The solution is decanted and filtered from the precipitated calcium sulphate, evaporated and crystallised and the crystals dissolved and recrystallised. Methods (2) and (3) are used on the manufacturing scale.

Sodium acetate forms monoclinic crystals, containing 3 molecules of water; strong saline taste; soluble in 2.8 cold water and in about 0.5 boiling water. The crystals melt completely



at 75°C. and lose their water of crystallisation at 100°C. By solution of this salt in ordinary strong acetic acid and rapid evaporation the diacetate of soda is formed; when glacial acid is used the triacetate is produced.

Sodium acetate is used for the preparation of acetic acid and in medicine; for the preservation of meat and other foods instead of salt. The saturated solution is occasionally used for filling railway foot-warmers.

The commercial acetate is liable to contain sulphates, chlorides and carbonates, and metallic salts. Tarry matters are frequently present from the pyroigneous acid used in its manufacture. Acetate of lime, and sulphate and carbonate of potash are occasionally added as adulterants.

#### ALKYL ACETATES. *Acetic ethers.*

Acetic acid forms numerous acetates with organic radicals. Some of these occur in the oils from various seeds.

#### Amyl acetates $C_5H_{11}(C_2H_3O_2)$ or $Ay(C_2H_3O_2)$ .

The following isomeric amyl acetates are known:—

1. Normal amyl acetate, boiling at 147-6° (Gartenmeister), at 148-4° (737 mm.) (Lieben and Rossi).

2. Iso-amyl acetate.

3. Methyl propyl carbonyl acetate, boiling at 133°-135° (Wurtz), at 134°-137° (Schorlemmer).

4. Methyl isopropyl carbonyl acetate, boiling at 125° (Wurtz).

5. Diethyl carbonyl acetate, boiling at 132° (741 mm.) (Wagner and Saytzeff).

6. Tertiary amyl acetate, boiling at 124° (750 mm.) (Flavitzky).

Of these, only the second is of technical interest.

**Isoamyl acetate**, generally known as *amyl acetate* ( $CH_3CH_2CH_2CH_2C_2H_3O_2$ ), is a colourless liquid of an odour resembling that of Jargonelle pears. Sp.gr. 0.8762 $^{15^\circ}$  (Mendelëef), 0.8552 $^{20^\circ}$  (Brühl), b.p. 138.5°-139° at 758.6 (Schiff).

It may be prepared by distilling a mixture of 1 part amyl alcohol, 1 part strong sulphuric acid, and 2 parts dried potassium acetate. The distillate is agitated with water; the upper layer of purified amyl acetate is separated, shaken with a strong solution of sodium carbonate, again separated, dried over calcium chloride, and redistilled.

The commercial amyl acetate contains other of the isomers. It is prepared in a corresponding manner to the above, but ordinary purified fusel oil, which consists principally of a mixture of active and inactive primary iso-amyl alcohol, is substituted for the purer amyl alcohol, and calcium acetate is frequently used instead of the potassium salt.

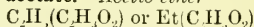
It is insoluble in water, but dissolves in all proportions in ether, amyl alcohol and ordinary alcohol. The latter solution is largely used under the name of Jargonelle pear essence for flavouring confectionery.

Camphor, tannin, resins, &c., dissolve readily in amyl acetate. A solution of gun-cotton therein is used as a varnish, for lacquering metals, &c., and in the form of a stiff jelly, mixed with opaque substances such as china clay, as a substitute for celluloid.

Whitley Williams has recommended its use

for the production of a standard flame in Photometry (J. S. C. I. 1885, 262).

#### Ethyl acetate. *Acetic ether*



is a fragrant limpid liquid of sp.gr. 0.9072 $^{15^\circ}$ , b.p. 77.5°C. (Perkin).

For the preparation of acetic ether 3.6 pts. by weight of commercial absolute alcohol is mixed with 9 pts. sulphuric acid with constant stirring. After standing twenty-four hours the mixture is poured on 6 pts. of fused sodium acetate (in small lumps), allowed to stand for twelve hours and distilled. The product is rectified over calcium chloride and carbonate of potash and redistilled. Clark recommends the following process: 233 c.c. (10 oz.) of rectified alcohol (sp. gr. 0.838) are placed in a flask, and 233 c.c. of sulphuric acid (B. P.) are added with constant stirring. The liquid should be cooled externally as far as possible, allowed to stand till the temperature has sunk to 15°C., and 351 grams (12½ oz.) of dried sodium acetate added gradually with constant agitation and cooling. The flask is then connected with a condenser and the liquid distilled until 400 c.c. (14 oz.) has distilled over; this is digested for three days with 2 oz. freshly-dried potassium carbonate and filtered. The filtrate is distilled on the water bath until all but 1 oz. has passed over. On the large scale dried sodium acetate may be substituted for the potassium carbonate with a disadvantage (v. further W. I. Clark, Ph. [3] 1883, 777).

Ethyl acetate is soluble in 8 parts of water at 0°C. and somewhat less soluble in water at 15°C. On the other hand, 1 part water dissolves in 25 parts of the acetate at 0°C. and in 24 parts at 15°C.

Commercial acetic ether usually contains less than 75 p.c. of real ethyl acetate, the rest being acetic acid, alcohol, water, ether, &c. It occurs, together with other organic acetates, in vinegar and wines.

**Methyl acetate**  $CH_3C_2H_3O_2$  or  $Me(C_2H_3O_2)$  is a colourless fragrant liquid of specific gravity 0.9398 $^{15^\circ}$ , boiling at 57.5°C. (760 mm.) (Perkin). It occurs in wood-spirit, and in crude wood-vinegar.

Methyl acetate is best prepared by distilling a mixture of 1 part methyl alcohol, 1 part potassium acetate, and 2 parts sulphuric acid. The product is dried over calcium chloride and quicklime and redistilled. It is soluble in water, alcohol, and ether.

**ACETOMETER.** A hydrometer graduated to indicate the strength of commercial acetic acid according to its density.

**ACETONE**  $C_3H_6O$  or  $CH_3.CO.CH_3$ . *Dimethyl ketone.* A product of the destructive distillation of acetates; obtained by Liebig from lead acetate (A. 1, 225) and further examined by Dumas (A. Ch. [2] 49, 208), who first determined its composition. Acetone is also produced in the dry distillation of wood (Völkell, A. 80, 310), of citric acid (Robiquet, B. J. 18, 502), of sugar, starch, and gums with lime (Frémy, A. 15, 279), and by heating citric acid with potassium permanganate (Péan de St. Gilles, J. 1858, 585).

*Preparation.*—1. Acetone can be obtained by distilling a mixture of 1 part of caustic lime and 2 parts of crystallised lead acetate (Zeise, A. 33, 32); but is usually prepared by the dry dis-

tillation of barium acetate at a moderate heat. Calcium acetate can also be employed, but the temperature required is greater, and the product is contaminated with impurities, such as dumasine, an isomeride of mesityl oxide.—2. From wood-spirit acetone can be separated by distilling over calcium chloride. The product obtained by these methods can readily be purified by converting the acetone into its crystalline compound with acid sodium (or potassium) sulphite, crystallising this, and subsequently distilling with aqueous sodium carbonate; the distillate is then treated with concentrated calcium chloride solution and the ethereal layer rectified over solid chloride.

Acetone has been prepared synthetically from zinc methyl and acetyl chloride (Freund, A. 118, 11). Occurs in the urine, blood, and brain of calcium diabetic patients.

*Properties.*—Acetone is a limpid, mobile liquid, having an agreeable odour and a peppermint-like taste. It is very inflammable and burns with a white smokeless flame. Its b.p. =  $56^{\circ}30'$  (Regnault); b.p. =  $56^{\circ}32'$  at 760 mm., and sp.gr. = 0.8144 at  $0^{\circ}$ ; = 0.79945 at  $13^{\circ}9'$  (Kopp, A. 64, 214; b.p. =  $56^{\circ}53'$  (cor.) and sp.gr. = 0.81853 at  $15^{\circ}$  (Thorpe, C. J. 37, 212). Acetone is miscible in all proportions with water, alcohol, ether and many ethereal salts, can be separated from its aqueous solution by the addition of calcium chloride, and dissolves many fats and resins. When its vapour is passed through a red-hot copper tube, a very small proportion of tarry products containing naphthalene is obtained together with a large volume of gas having the composition: carbon monoxide = 39.23 per cent.; methane = 37.58 per cent.; hydrogen = 17.54 per cent.; and ethylene = 5.65 per cent. (Barbier and Roux, C. R. 102, 1559). Dehydrating agents readily act on acetone and convert it into condensation compounds; thus, for example, caustic lime converts acetone into mesityl oxide  $C_8H_{10}O$  and phorone  $C_8H_{14}O$  when the action is allowed to continue for a week (Fittig, A. 110, 32), and, together with smaller proportions of other products, these two compounds are also formed when it is saturated with hydrogen chloride and allowed to stand for eight to fourteen days (Baeyer, A. 140, 207). Distillation with concentrated sulphuric acid converts acetone into mesitylene. Sodium in the presence of water reduces acetone to isopropyl alcohol and pinacol (Fittig, A. 110, 25; 114, 54; Städeler, A. 111, 277; Friedel, A. 124, 329); whilst chlorine, bromine and iodine in the presence of alkalis convert it into chloroform, bromoform, and iodoform respectively.

*Reactions.*—Acetone, when treated with aqueous potash and iodine, yields iodoform (Lieben). Gunning (Z. Fr. 24, 147) has modified this reaction to render it available when alcohol is present in the substance suspected to contain acetone, and employs ammonia and a solution of iodine in ammonium iodide. Another test proposed by Reynolds (Fr. 24, 147) is based on the fact that mercuric oxide is soluble in acetone in the presence of potassium hydroxide; the suspected liquid is mixed with a solution of mercuric chloride rendered strongly alkaline with alcoholic potash, and after shaking the mixture

is filtered and the filtrate tested for mercury by means of ammonium sulphide or stannous chloride. Penzoldt (Fr. 24, 147) adds to the suspected liquid orthonitrobenzaldehyde, which in presence of caustic alkali combines with acetone to form indigo. Jacksch (C. C. 1884, 674) states that Lieben's test is the most sensitive, and that by its use 0.00001 gram of acetone can be detected, also that the degree of delicacy of the other tests stands in the order in which they are given here.

*Derivatives.*—Acetone combines directly with a large number of substances yielding well-characterised additive compounds.—1. Compounds with alkaline sulphites:—Acetone forms definite crystalline compounds when shaken with concentrated solutions of the acid sulphites (bisulphites) of the alkali metals. The potassium salt,  $C_3H_7O.KHSO_3$ , and the sodium salt,  $C_3H_7O.NaHSO_3$ , crystallise in nacreous scales (Limpriecht, A. 93, 238); the ammonium salt,  $C_3H_7O.NH_4HSO_3$ , crystallises in laminae (Städeler, A. 111, 307). These salts yield acetone when heated with aqueous potash.—2. Compounds with chloroform (Willgerodt, B. 14, 2451; 15, 2308). 3. Compounds with hydrogen cyanide (Urech, A. 164, 255):—Acetone yields acetonecyanhydrol  $C_4H_7NO$ , b.p. =  $120^{\circ}$ , when added to anhydrous hydrogen cyanide; and diacetonecyanhydrol  $C_6H_{11}NO_2$ , a crystalline substance, when treated with a 25 per cent. solution (aqueous) of hydrogen cyanide (Tiemann and Friedländer, B. 14, 1965).—4. Compounds with ammonia:—Ammonia unites with acetone in the cold with the elimination of the elements of water; the reaction, however, proceeds more quickly if the temperature is raised to  $100^{\circ}$ , or if dry ammonia gas is passed into boiling acetone. Several bases, diacetoneamine  $C_6H_{11}NO$ , triacetoneamine  $C_8H_{17}NO$ , triacetonediamine  $C_8H_{19}N_2O$ , and dehydrotriacetoneamine  $C_8H_{15}N$ , the last two in very small quantity only, have been obtained by these methods, the relative proportions in which they are formed varying with the temperature employed and the duration of the experiment. These bases and their derivatives have been examined by Heintz (A. 174, 133; 175, 252; 178, 305, 326; 181, 70; 183, 276; 189, 214; 191, 122; 198, 42, 87; 201, 90; 203, 336) and also by Sokolow and Latschinow (B. 7, 1384); they yield well-crystallised salts, and can be separated from one another by means of their oxalates. Methylamine also gives corresponding compounds with acetone, but dimethylamine yields dimethylacetoneamine as the sole product (Göttschmann, A. 197, 27).

Acetone also yields substitution derivatives when acted upon with chlorine (Bischoff, B. 5, 863, 963; 8, 1329) and bromine. By the direct action of chlorine, monochloroacetone (Henry, B. 5, 190; Mulder, B. 5, 1009; Barbaglia, B. 7, 467; Linnemann, A. 134, 171); unsymmetrical dichloroacetone (Fittig, A. 110, 40; Borsche and Fittig, A. 133, 112); symmetrical dichloroacetone (Barbaglia, *l.c.*); trichloroacetone (Bischoff, *l.c.*; Kraemer, B. 7, 252); tetrachloroacetone (Bischoff) and pentachloroacetone (Clocz, Bl. 39, 638) are obtained; and the corresponding bromo-derivatives, with the exception of tribromoacetone, are obtained by the direct action of bromine upon acetone (Mulder, J. 1861, 330).



**ACETOPHENONE.** *Phenyl-methyl-ketone.*  
*Hyppnone.*  $C_6H_5.CO.CH_3$ .

Is obtained by acting with benzoyl chloride on zinc methyl; by distilling a mixture of the calcium salts of benzoic and acetic acids, or by boiling together benzene and acetyl chloride with aluminium chloride.

Crystallises in large plates which melt at  $20.5^\circ$ . Boils at  $202^\circ$ . It possesses a persistent odour of oil of bitter almonds and cherry laurel water; is insoluble in water, but dissolves easily in alcohol, ether, chloroform, or benzene. Was discovered by Dujardin-Bearmetz and Bardet to possess powerful soporific properties (C. R. 101, 960). Used in quantities of .05 to .15 grains it induces a quiet sleep, but is said to impart a disagreeable odour to the breath (Ph. 1886, 582).

**$\beta$ -ACETO-PROPIONIC ACID.** *Levulinic acid.*  
 $CH_3.CO.CH_2.CO_2H$ .

This substance is formed by the action of dilute acids on a number of carbohydrates—e.g. levulose, inulin, galactose—but is best prepared by heating on the water-bath cane sugar with dilute hydrochloric acid (4 vols. water, 1 vol. conc. acid) until a brown flocculent precipitate is no longer formed. Compare Tollens, B. 17, 668; Wehmer a. Tollens, A. 243, 214. The filtered liquid is then evaporated on the water-bath, extracted several times with ether, and after distilling off the ether the residue is fractionated in a vacuum.

Levulinic acid crystallises in plates which melt at  $33^\circ$ . It boils at  $239^\circ$ , and has at  $15^\circ$  a sp.gr. 1.135. It is very soluble in water, alcohol, and ether, and is not attacked by bromine in the cold. Nitric acid converts it into carbon dioxide, acetic acid, succinic and oxalic acids. Iodine and sodic hydrate form iodoform even in the cold. Hydriodic acid and phosphorus at  $200^\circ$  convert it into normal valeric acid; whereas sodium amalgam forms sodium  $\gamma$ -hydroxyvalerate acid in an alcoholic solution, and normal valeric acid in an acid solution.

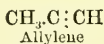
The substance is employed on a manufacturing scale as a mordant instead of acetic acid, as it possesses the advantage of not being volatile with steam.

It is also used in the preparation of the antipyretic 'antithermin.' Phenylhydrazine is dissolved in dilute acetic acid, and on adding a solution of levulinic acid a yellow precipitate is formed, which is purified by recrystallisation from alcohol (Ph. [3] xvii. 801) (v. ANTITHERMIN).

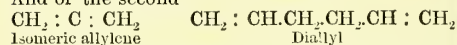
**ACETPHENETIDENE** v. PHENACETIN.

**ACETYLENE GROUP.** Hydrocarbons having the general formula  $C_nH_{2n-2}$ .

The hydrocarbons of this series exist in two isomeric modifications. Representatives of the first group are



And of the second

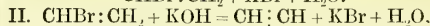
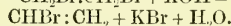
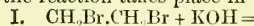


The hydrocarbons of the first group thus contain the group ( $\equiv CH$ ) united to one carbon atom, and may be designated true acetylenes. They form compounds with copper and silver in which the hydrogen of the group ( $CH$ ) is replaced by the metal.

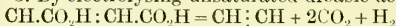
The following general reactions yield hydrocarbons of this series:—

1. By heating the monohalogen derivatives of the hydrocarbons  $C_nH_n$  with alcoholic potash  $CH_3.CCl:CH_2 + KOH = CH_2.C:CH + KCl + H_2O$ .

2. By the action of alcoholic potash on the dihalogen derivatives of the ethylene series. In this case the reaction takes place in two stages.



3. By electrolysis unsaturated dibasic acids.

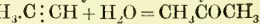
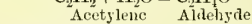
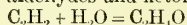


Fumaric acid                      Acetylene

The acetylenes combine with  $Br_2$  or  $BrI$ ; thus acetylene forms  $C_2H_2Br_2$  and  $C_2H_2BrI$ .

Nascent hydrogen converts the acetylenes into the hydrocarbons  $C_nH_{2n}$  and  $C_nH_{2n+2}$ .

The acetylenes also in presence of mercuric bromide and other mercuric salts combine with water to form aldehydes and ketones.



(Kutscheroff, B. 14, 1542; 17, 28).

By polymerisation of the acetylenes bodies of the benzene series are formed. Thus acetylene at a red heat yields benzene; allylene  $C_3H_4$ , by the action of sulphuric acid, gives mesitylene  $C_6H_6$  (trimethyl benzene); and crotonylene  $C_4H_4$  gives hexamethyl benzene.

**Acetylene**  $C_2H_2$  i.e.  $HC:CH$  is produced when an electric arc is formed between carbon points in an atmosphere of hydrogen. Further by passing the vapours of many carbon compounds (alcohol, ether, methane, ethylene) through red-hot tubes. It is also formed by electrolysis the sodium or potassium salt of fumaric or maleic acid, and by the action of silver, copper, or zinc dust on iodoform (Cazeuve, C. R. 97, 1371). (For other modes, v. WATTS' DICTIONARY OF CHEMISTRY.)

To prepare larger quantities, ethylene bromide  $C_2H_4Br_2$  is heated with potash and strong alcohol in a flask with an inverted condenser. The gas is passed into ammoniacal solution of cuprous chloride, and the precipitate, after washing with water, is decomposed by hydrochloric acid. Or a Bunsen burner is allowed to strike back, and the gases are drawn through the cuprous chloride solution.

Acetylene is a colourless gas which has a peculiar odour, and condenses at  $+1^\circ$  at a pressure of 48 atmospheres. It is slightly soluble in water, more so in alcohol and ether. The gas burns in air with a smoky flame.

On heating sodium in acetylene hydrogen is given off, and the compounds  $C_2HNa$  and  $C_2Na_2$  are formed.

The compounds with copper and silver correspond respectively to the formulæ  $C_2H.Cu_2O$  and  $C_2H.Ag_2O$ , or  $C_2H_2.2Ag_2O$ . The former is red, the latter yellowish. Both explode on heating (Bloelmann, A. 173, 174).

Nascent hydrogen converts acetylene into  $C_2H_4$  and  $C_2H_6$ . The latter gas is also formed by passing hydrogen and acetylene over spongy platinum. A mixture of nitrogen and acetylene

<sup>1</sup> Since coal gas contains acetylene (.06 p.e.) copper tubes cannot be used for gas service pipes (Beilstein).

subjected to the action of induction sparks yields prussic acid  $C_2H_2 + N_2 = 2HCN$  (Beilstein).

Chlorine and acetylene combine explosively when exposed to daylight. Antimony pentachloride when gently heated absorbs acetylene, forming  $C_2H_2SbCl_5$ , which, on distillation, decomposes into  $SbCl_5$  and  $C_2H_2Cl_2$ .

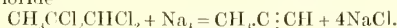
Bromine added to an alcoholic solution of acetylene forms  $C_2H_2Br_2$ , but if the gas be passed through bromine the substances  $C_2H_2Br$ , and  $(C_2HBr)_n$  are obtained. Iodine forms  $C_2H_2I_2$ .

**Allylene or Allene**  $C_3H_4$  exists in two isomeric modifications.

1. *Methyl acetylene*  $CH_3C \equiv CH$ .

Is formed by the action of alcoholic potash on bromopropylene.

$CH_3CClCH_2 + KOH = CH_3C \equiv CH + KCl + H_2O$ . Also by acting with sodium on dichloroacetone chloride



By electrolysis the alkali salts of citraconic or mesaconic acids.

The substance is a colourless gas very similar to acetylene, and, like it, forms compounds with metals. The mercuric compound is obtained by passing allylene through water containing mercuric oxide in suspension. It has the composition  $(C_3H_4)_2Hg$ , and crystallises from hot alcohol in fine needles. It is soluble in hydrochloric acid with evolution of allylene, but does not explode on heating.

$(C_3H_4)_2Ag$  forms microscopic needles which explode at about  $150^\circ$ .

Bromine forms the additive products  $C_3H_4Br$ , and  $C_3H_4Br_2$ , and the halogen acid compounds corresponding to  $CH_3CCl_2CH_2$ . Concentrated sulphuric acid absorbs allylene easily. On distilling the solution with water, acetone, mesitylene and allylenesulphonic acid  $C_3H_4SO_3H$  are formed (Schrode, B. 8, 18 and 367).

The formation of acetone from allylene in presence of mercuric salts in water has been alluded to above.

2. *Symmetrical allylene*  $CH_2 : C : CH_2$ .

Is obtained by the action of sodium on  $\beta$ -chlorallylchloride.

$CHCl : CH : CHCl + 2Na = CH_2 : C : CH_2 + 2NaCl$ . Or by the action of Zn dust on an alcoholic solution of dibrompropylene (Gustavson and Demjanoff, J. pr. 1888, 201). And by the electrolysis of the alkali salts of itaconic acid.

The substance is a gas, but differs from unsymmetrical allylene in giving no precipitate with an ammoniacal copper or silver solution. It unites with bromine to form  $C_3H_4Br_2$ , which melts at  $195^\circ$ .

**Butines**  $C_4H_6$ .

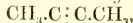
Three of the four possible isomerides are known.

1. *Ethylacetylene*  $C_2H_5C \equiv CH$ . Formed by the action of alcoholic potash on  $C_2H_5CCl_2CH_3$  (Bruylants, B. 8, 412).

By passing acetylene and ethylene through a red-hot tube (Berthelot, A. Ch. [4] 9, 466).

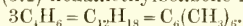
The compound is a liquid boiling at  $18^\circ$ , and is a true acetylene, since it forms precipitates with ammoniacal copper and silver solutions.

2. *Crotonylene or dimethylacetylene*



by acting with alcoholic potash on  $\psi$ -butylene bromide  $CH_3CHBrCHBrCH_3$ ; is a liquid boiling

at  $18^\circ$ . It forms with bromine a liquid  $C_4H_6Br_2$  (b.p.  $148^\circ$ - $158^\circ$ ), and  $C_4H_6Br_4$ , which is solid. On shaking the hydrocarbon with sulphuric acid and water (3:1) hexamethylbenzene is obtained



3. *Vinyl-ethylene*  $CH_2 : CH : CH : CH_2$ . By passing the vapours of fusel oil through a red-hot tube (Caventou, A. 127, 348). Is present in compressed coal-gas (Caventou, B. 6, 70), and in oil-gas (Armstrong and Miller, C. J. 1886, 74). It gives no precipitate with an ammoniacal cuprous chloride solution, but forms an additive product with four atoms of chlorine or bromine.

4. The butine  $CH_3CH : C : CH_2$  is unknown.

Four of eight possible pentines are known. Of the higher terms of the series the *hexine diallyl* is of interest. It is formed by the action of sodium on allyl iodide.

$2C_3H_5 : CH : CH_2I + 2Na = CH_2 : CH : CH_2CH_2CH : CH_2 + 2NaI$ . Also by distilling mercuric allyl iodide with potassium cyanide.

It forms a liquid smelling of horse-radish, boiling at  $59^\circ$ , and combines with bromine to form the tetrabromide  $C_6H_8Br_4$ , melting at  $63^\circ$ . If this be boiled with potash a liquid dibromodiallyl is obtained, which boils at  $210^\circ$ , and by the action of alcoholic potash yields *dipropargyl*  $C_6H_6$ , a liquid boiling at  $85^\circ$  isomeric with benzene, but having the constitution



**ACHREMATITE** A molybdo-arsenate of lead from Guanacere in the State of Chihuahua, Mexico. It contains  $As_2O_5$ , 18.25;  $MoO_3$ , 5.01;  $Cl$ , 2.15;  $Pb$  (as chloride), 6.28;  $PbO$  remaining 68.31 (Mallet, C. S. J. 1875, 1141).

**ACHYRANTHES ASPERA** or **AGHARA**.

An Indian plant used as a simple and as a remedy for toothache.

**ACICULITE**. *Bismuthsulphide* (v. **BISMUTH**).

**ACID ALBUMEN** v. **ALBUMINOIDS**.

**ACID BROWN** v. **AZO-COLOURING MATTERS**.

**ACID CERISE** v. **TRIPHENYLMETHANE COLOURING MATTERS**.

**ACID GREEN** v. **TRIPHENYLMETHANE COLOURING MATTERS**.

**ACIDIMETRY AND ALKALIMETRY**. The determination of the amount of acid or alkali in solid and liquid substances. If the substance is a liquid free from admixed foreign matter, the proportion of acid or alkali can be ascertained with considerable accuracy by determining the specific gravity of the solution. A direct determination can also be made by any suitable gravimetric process; but volumetric methods are almost exclusively employed, and, indeed, are the only processes available when it is required to distinguish between free and combined acid or alkali. In these processes the quantity of acid or alkali present is calculated from the volume of standard alkali or acid required to exactly saturate it, the point of saturation being determined by means of an *indicator*—i.e. a substance which gives a decided colour change with a slight excess of acid or alkali.

The basis upon which the standard solutions are made is normal sodium carbonate, which is purified by recrystallisation and rendered anhydrous by careful heating in a platinum vessel. It can also be prepared by heating pure sodium-hydrogen-carbonate until it ceases to lose weight. Mohr recommends crystallised oxalic acid as a



basis; but it is not easy to obtain crystals having exactly the composition  $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$ , and the solution is not available for general purposes.

**Preparation of the Standard Acid.**—Sulphuric or hydrochloric acid is generally used. The former has the advantage of being completely non-volatile in dilute solutions, whilst the latter gives no precipitates with compounds of calcium, barium, and strontium. Nitric acid has also been proposed, but it has no advantages over sulphuric and hydrochloric acids, is not so readily obtained pure, and is liable to decompose, especially if exposed to bright light.

**Sulphuric acid.**—28 c.c. of the pure concentrated acid, of sp.gr. 1·84, diluted to 1000 c.c., gives an approximately normal solution—that is, a solution which contains in each litre one equivalent of the acid in grams.

**Hydrochloric acid.**—Advantage is taken of the fact that an aqueous solution of hydrochloric acid, which boils at a constant temperature under the ordinary atmospheric pressure, has a practically constant composition. A quantity of the ordinary concentrated acid is placed in a capacious retort and distilled until about one-third has passed over. The liquid remaining in the retort will have a sp.gr. of 1·1, and will contain 20·2 p.c. of real acid. 165 c.c. of this acid diluted to 1000 c.c. gives an almost exactly normal solution. A quicker method is to determine the strength of the concentrated acid by taking its sp.gr. by a hydrometer, and then dilute a sufficient quantity to 1000 c.c.

The final adjustment of the acid in either case is made by means of sodium carbonate. About 1 gram of the pure anhydrous salt is accurately weighed into a flask of about 250 c.c. capacity, dissolved in water, and mixed with a few drops of litmus solution. The acid is placed in a burette graduated in fifths or tenths of a cubic centimetre, and is gradually added to the carbonate solution until the colour of the litmus changes to wine-red. The solution is now boiled for a few minutes to expel carbon dioxide, a further small quantity of acid is added and the liquid again boiled, and this process is continued until the litmus remains red after boiling for some minutes. The volume of acid used is read off, and the experiment is repeated with a fresh quantity of the carbonate. The quantity of hydrochloric or sulphuric acid required to saturate the weight of sodium carbonate taken is calculated, and this quantity divided by the number of c.c. of acid used gives the amount of real acid in 1 c.c. of the solution. Suppose that a solution of sulphuric acid is being standardised, and that 18 c.c. are required to saturate 1·025 gram of sodium carbonate.  $106 : 1·025 :: 98 : 0·9476$ , and therefore 1 c.c. of the acid contains  $·9476 \div 18 = 0·0526$  gram  $\text{H}_2\text{SO}_4$ . It follows that 931·5 c.c. of this acid contain 49 grams  $\text{H}_2\text{SO}_4$ ; and if this volume is diluted to 1000 c.c., the resulting solution should be exactly normal. To adopt a more convenient plan: 1000 c.c. of the solution contain 52·6 grams  $\text{H}_2\text{SO}_4$ , an amount of acid which would be contained in 1073·5 c.c. of a strictly normal solution ( $49 : 52·6 :: 1000 : 1073·5$ ), and hence, to obtain a normal solution, 1000 c.c. of the acid must be mixed with 73·5 c.c. of water. Whichever method is adopted, the accuracy of the solution

must be confirmed by again standardising with sodium carbonate. Since the accurate adjustment to normal strength is troublesome, it is better to determine the error of the solution and to make a correction for this error in each calculation. The actual strength of the solution ( $x$ ) is divided by the equivalent of the acid, and the resulting number  $\frac{x}{\text{equivalent}} = f$  is a factor which

denotes the deviation of the acid from the normal strength. In the example given  $\frac{52·6}{49} = 1·074$ —

that is to say, 1 c.c. of solution contains  $0·049 \times 1·074$  gram  $\text{H}_2\text{SO}_4$ , and is therefore equivalent to  $0·040 \times 1·074$  gram of sodium hydroxide,  $0·053 \times 1·074$  gram of sodium carbonate,  $0·017 \times 1·074$  gram of ammonia, and so on.

Since the repeated boiling required when the carbonate is directly titrated makes the operation very tedious, it is better to adopt the process of reverse titration. The relation between the acid and the standard caustic alkali is first determined by direct titration, boiling being unnecessary. About 1 gram of sodium carbonate is weighed out, dissolved in water, mixed with a measured excess (25 c.c.) of standard acid, boiled for about ten minutes to expel all carbon dioxide, mixed with litmus, and the excess of acid determined by adding the standard alkali from the burette until the litmus becomes blue. The volume of alkali required gives the excess of acid, and this subtracted from the volume of acid added, gives the volume required to neutralise the sodium carbonate taken. Suppose that 10 c.c. of alkali = 10·2 c.c. of acid, and that 1·025 gram of sodium carbonate, after boiling with 25 c.c. of the acid, required 6·9 c.c. of alkali to neutralise the excess of acid. 6·9 c.c. of alkali = 7·0 c.c. of acid, and therefore  $25 - 7 = 18$  c.c. of acid have been required to neutralise 1·025 gram of sodium carbonate. The strength of the acid is then calculated in the manner already explained.

**Oxalic acid.**—A normal solution is prepared by dissolving 63·00 grams of the recrystallised hydrated acid  $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$  in water and diluting to 1000 c.c.

**Preparation of Standard Alkali.**—The alkali generally used is normal sodium or potassium hydroxide, or half-normal ammonia.

50 grams of the purest commercial caustic soda is dissolved in 800–900 c.c. of water, allowed to stand for some time in order that any insoluble matter may subside, and the clear liquid is siphoned off and diluted to 1000 c.c. 10 c.c. of standard acid is placed in a porcelain dish, mixed with litmus, and the alkali added from a burette until the litmus becomes blue. If 9·4 c.c. of alkali are required, it follows that 940 c.c. of alkali are equivalent to 1000 c.c. of acid, and this volume of alkali should be diluted to 1000 c.c., or 1000 c.c. of alkali should be mixed with 64 c.c. of water ( $9·4 : 10 :: 1000 : 1064$ ). The ratio of the diluted alkali to the standard acid is again determined, and the strength of the alkali is readily calculated.

Ammonia has the advantages that it does not readily attack glass, is free from silica and alumina, and does not so readily absorb carbon dioxide from the air. If used of half-normal

strength it does not appreciably alter if kept in a cool place. All titrations must, however, be made in cold solutions, and phenol phthalein cannot be used as an indicator, 25 c.c. of ammonia solution of sp.gr. 0.89 is diluted to 1000 c.c., and the solution adjusted exactly as in the case of soda.

**INDICATORS.**—Many colouring matters, both natural and artificial, have been recommended for this purpose, but comparatively few are actually used.

**Litmus** occurs in the form of small cubical granules mixed with a large proportion of calcium carbonate. An aqueous solution of this product not only contains free alkali, but also a variable proportion of colouring matters which interfere with the delicacy of the reaction. Special precautions must therefore be taken in preparing the solution for use in acidimetry. Various processes have been recommended by Berthelot and De Fleuriën (*A. Ch.* [4] 5, 189), Wartha (*B.* 9, 217), Kretzschmar (*C.Z.* 3, 682), Stolba (*C. C.* [3] 12, 770), Mohr (*Titrimethode*). The following method gives excellent results: The litmus is extracted three or four times with boiling methylated alcohol of 85 p.c. in order to remove the injurious colouring matters, the residue is extracted with cold water, slightly acidified with sulphuric acid, and boiled to expel carbon dioxide. It is then neutralised with baryta water, a few bubbles of carbon dioxide passed in to remove excess of baryta, again boiled and filtered. The solution should contain about 20 grams of solid matter per litre, and must be kept in vessels to which the air has free access, for if kept in closed vessels it undergoes fermentation and is decolourised. The colour is restored when the liquid is exposed to air. It has been recommended to evaporate the solution to dryness at 90° and dissolve the residue in glycerol (*Ph. Centralhalle*, N.S. 3, 171). The colour of the solution should be purple; it turns blue with alkalis, and red with acids, and is affected by carbon dioxide, sulphur dioxide, and hydrogen sulphide. In order to avoid the slight error due to the fact that a small quantity of acid or alkali is required to produce the colour change, Mohr recommends the use of red litmus in cases where the end reaction will be red, and blue litmus in cases where the end reaction will be blue. He also recommends the addition of litmus to the bulk of the standard acid and alkali in order to avoid mistakes in using them.

The colour change is rendered more delicate by conducting the titration in the monochromatic light obtained by heating a bead of sodium carbonate in a Bunsen flame (*L. Henry*, *C.R.* 76, 222). The red solution seems colourless, whilst the blue solution is almost black.

**Cochineal** was first recommended by Luckow (*J. pr.* 84, 424; *Fr.* 1, 386). 3 grams of the substance, which should not be pulverised, is extracted with 250 c.c. of a mixture of 1 volume of alcohol with 3.4 volumes of water. It is yellowish-red with acids, and purple with alkalis, and is not affected by carbon dioxide. It is highly sensitive, and can be used in very dilute solutions. With this indicator the carbonates of the alkaline earths have an alkaline reaction.

**Methyl orange**, or Poirrier's Orange III. (Dimethylanilinediazobenzenesulphonic acid), recommended by W. v. Miller (*B.* 11, 460; see also Lunge, *B.* 11, 1944; *S. C. I.* 1, 16), has the advantage that it is not affected by carbon dioxide or hydrogen sulphide, and the alkaline carbonates and sulphides can therefore be titrated in the cold. The presence of normal alkaline salts affects the delicacy of the reaction, and 0.1–0.3 c.c. of normal acid is required to produce the colour change. 1 gram of the substance is dissolved in 1000 c.c. of water. It is pale-yellow in alkaline solutions, and pink with acids; it is neutral to many normal salts which are acid or alkaline to litmus.

**Phenol phthalein**, obtained by heating phenol with phthalic anhydride and sulphuric acid (Baeyer, *A.* 202, 69), is extremely sensitive to alkalis, with which it gives a red colour, and can be used in very dilute solutions (*E. Luck*, *Fr.* 16, 322). It is, however, affected by carbon dioxide and sulphur dioxide, hydrogen sulphide, &c. With excess of acid the solution is colourless. One gram of the phenol phthalein is dissolved in 500 c.c. of dilute alcohol.

**Aurin**, obtained by the action of sulphuric acid on a mixture of oxalic acid and phenol, is colourless with acids, but pink with alkalis. It is very sensitive, and is especially useful in the titration of dilute solutions of barium hydroxide, as in Pettenkofer's method for the estimation of carbon dioxide in the air. It is affected by carbon dioxide and hydrogen sulphide. One gram of the aurine is dissolved in 500 c.c. of dilute alcohol.

**Phenacetolin**, recommended by Degener (*Zeit. d. Ver. f. d. Rübenzucker Industrie*, 1881, 357; *S. C. I.* 1, 85), is prepared by boiling together for several hours equal molecular proportions of phenol, acetic anhydride, and sulphuric acid. The product is extracted with water to remove excess of acid, dried and dissolved in alcohol in the proportion of 1 gram to 500 c.c. It is pale-yellow with alkalis, red with carbonates of the alkalis and alkaline earths, colourless with acids.

**Lackmoid**, a colouring matter very similar to litmus, is obtained by heating gradually to 110°C. a mixture of 100 parts resorcinol, 5 parts sodium nitrite and 5 parts water. When the violent reaction moderates, the mass is heated to 115°–120° until evolution of ammonia ceases. The product is a glistening reddish powder, insoluble in chloroform, benzene, and light petroleum, easily soluble in methyl, ethyl, and amyl alcohol, less soluble in water and ether (*M. C. Traub* and *C. Hock*, *B.* 17, 2615). Its colour changes are similar to those of litmus, but it is more sensitive. One gram of lackmoid is dissolved in 500 c.c. of dilute alcohol.

**Turmeric** contains a yellow colouring matter which gives a dark-brown colouration with alkaline hydroxides and may be used in the form of paper in titrating with caustic alkalis (Pettenkofer). The root is extracted with water in order to remove a yellow colouring matter insensitive to alkalis, and the residue is treated with alcohol. Strips of unsized paper are steeped in the alcoholic solution and dried.

Other indicators which have been proposed, but which have no special advantages and have not come into general use, are hematoxylin



(Wildenstein, Fr. 2, 9); cyanin (Schönbein, J. pr. 95, 449); tincture of barwood (Stolba, Fr. 14, 324); alizarin (Schaal, B. 6, 1180); fluorescein (Krüger, B. 9, 1572); ferric salicylate (Weiske, J. pr. N.S. 12, 157); tincture of oranges (Bornträger, Fr. 17, 459); flavescein (Lux, Fr. 19, 457); nitrophenol (Langbeck, C. N. 43, 161); the product obtained by fusing tetra-hydroelagic acid with potash (Oser and Kalmann, M. 2, 250); Poirrier's soluble blue C4B (Engel, C. R. 102, 214); dimethylazoamidobenzene (Fischer and Philipp, C. Z. 56, 998), and Congo red. Many of the azo-colours can likewise be used (W. v. Miller, B. 11, 460).

The indicators differ not only in the nature of the colour change, but also in their behaviour with different substances. Many normal salts which are acid or alkaline to litmus are neutral to methyl orange or phenol phthalein. Some substances which are acid to methyl orange are neutral to phenol phthalein, and so on.

The relative sensitiveness of the more important indicators and their behaviour under various conditions have been investigated by Wieland (B. 16), and especially by Thomson (C. N. 47, 123, 135, 184; 49, 32, 38, 119; 52, 18, 29), whose results are summarised in the following table:—

	Litmus	Lackmoid	Aurin	Methyl Orange	Phenacetolin	Phenolphthalein
	0.05	0.01	0.01	0.05	0.01	0.01
Sensitiveness . . .	Available	Available	—	—	—	—
Hot solutions . . .	Available	Available	—	—	—	—
Ammonia . . . . .	Available	Available	Available	Available	Available	Not available
Ammonium salts . . .	Not affected	Not affected	Less sensitive	Less sensitive	Not affected	Not available
Neutral alkaline salts .	Not affected	Not affected	Not affected	Less sensitive	Not affected	Not affected
Carbon dioxide . . .	Indefinite	Indefinite	Indefinite	Not affected	Colour changed	Indefinite
Hydrogen sulphide . .	Indefinite	Decolourised	Indefinite	Not affected	Not affected	Indefinite
Alkaline carbonates . .	Indefinite	Indefinite	Indefinite	Alkaline	Red colour	Alkaline
Alkaline bicarbonates .	Indefinite	Indefinite	Indefinite	Alkaline	—	Neutral
Sulphites . . . . .	Indefinite	Alkaline	Neutral	Alkaline	Not available	Neutral
Acid sulphites . . . .	Indefinite	Neutral	Acid	Neutral	Not available	Acid
Silicic acid . . . . .	Neutral	Neutral	Neutral	Neutral	Neutral	Not available
Alumina . . . . .	Indefinite	Alkaline	Indefinite	Alkaline	Neutral	Neutral
Boric acid . . . . .	Indefinite	Indefinite	Indefinite	Neutral	Indefinite	Indefinite
Sodium thiosulphate .	Neutral	Neutral	Neutral	Neutral	Neutral	Neutral
Sulphides . . . . .	Alkaline	Not available	—	Alkaline	Alkaline	Alkaline
Hydrosulphides . . .	Indefinite	Not available	—	Alkaline	—	Neutral
Potassium nitrite . .	Neutral	—	Neutral	Destroyed	Neutral	Neutral
Oxalic acid . . . . .	Available	Not available	Available	Not available	Not available	Available
Phosphoric acid . . .	Indefinite	Monobasic	Indefinite	Monobasic	Indefinite	Dibasic
Arsenic acid . . . . .	Indefinite	Monobasic	Indefinite	Monobasic	Monobasic	Dibasic
Arsenious acid . . . .	Neutral	Neutral	Neutral	Neutral	Neutral	Indefinite
Phenol . . . . .	Neutral	Neutral	Neutral	Neutral	Neutral	Indefinite

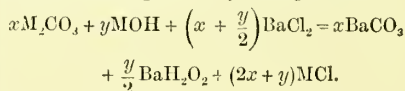
The sensitiveness is measured in c.c. of decinormal acid required to produce a distinct change when the volume of the liquid is 100 c.c. Where a reaction is given as 'indefinite,' it is not meant that there is no effect, but that the change is not sufficiently sharp to be available in analysis. In many cases where the reaction is indefinite in cold solutions it becomes definite if the liquid is boiled, *e.g.* litmus with sulphides, sulphites, and carbonates; phenol phthalein with sulphides and carbonates. Lackmoid is most serviceable in the form of paper, and several of the reactions which are unsatisfactory with the solution are sharp and distinct with the paper, *e.g.* with carbonates, sulphides and sulphites.

Gawalowski recommends (Fr. 22, 397) the use of a mixture of methyl orange and phenol phthalein, which is deep-red with excess of alkali, pale-yellow when neutral, and rose-red with excess of acid.

**Determination of total alkali.** A weighed quantity of the substance (10 grams) is dissolved in water, filtered if necessary, and diluted to 500 c.c. 50 c.c. is withdrawn, mixed with a measured excess (25 c.c.) of normal acid, boiled gently for ten minutes to expel carbon dioxide, and the excess of acid determined with standard alkali. The volume of standard acid minus the excess of acid gives the volume of acid required to neutralise the total alkali, *i.e.* the alkali present as hydroxide, carbonate, sulphide, sulphite, thiosulphate, aluminate and silicate. If methyl orange

is used as indicator, boiling is unnecessary, and the alkaline solution is titrated directly with standard acid. If direct titration with litmus as indicator is preferred, the solution must be boiled after each addition of acid in the manner described above for the preparation of the standard acid.

**Alkaline hydroxide in presence of carbonate.** 100 c.c. of the above solution is heated, mixed with excess of barium chloride, allowed to cool, diluted to 250 c.c. and well shaken. When the precipitate has settled, 50 c.c. of the clear liquid is withdrawn and titrated with standard acid. The quantity of acid used  $\times 25$  gives the volume equivalent to the hydroxide in the weight of substance originally taken. The reaction which takes place is expressed by the equation



The barium carbonate is precipitated and a quantity of barium hydroxide equivalent to the alkaline hydroxide remains in solution. The solution cannot be filtered, since the barium hydroxide would absorb carbon dioxide from the air with formation of the insoluble carbonate.

In order to avoid error due to the presence of the precipitate, and to economise time, Watson Smith (S. C. I. 1, 85) prefers to add just sufficient barium chloride to precipitate the carbonate without affecting the hydroxide. No

barium remains in solution, and even if carbon dioxide is absorbed the alkaline carbonate formed remains in solution. The barium chloride is added gradually to the hot solution until precipitation is just complete, and the liquid is filtered into a 250 c.c. flask and an aliquot portion titrated.

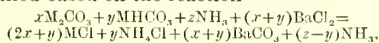
Thomson (*l.c.*) proposes to precipitate with excess of barium chloride, then add phenol phthalein and titrate at once with standard acid. The precipitated barium carbonate is, however, attacked by the acid, and hence the results are inaccurate.

**Carbonate in presence of hydroxide.** The solution is coloured a very faint yellow with phenacetolin, and standard acid is added until the yellow colour changes to a rose tint. The volume of acid required gives the amount of hydroxide present. A further quantity of acid is now added, and the red colour increases in intensity, but eventually changes to yellowish-red, and finally to golden-yellow. At this point a second reading is taken, and the difference between this and the first reading gives the volume of acid corresponding with the carbonate present (Lunge, S. C. I. 1, 56). This method is not available for the estimation of small quantities of hydroxide in presence of large quantities of carbonate (Thomson).

In order to estimate the proportion of carbonate in quick-lime or slaked lime, the purpose for which phenacetolin was originally recommended by Degener, 100-150 grams of the lime is made into a cream with water and diluted to 500 c.c. After vigorous agitation 100 c.c. is withdrawn and diluted to 1,000 c.c., and 25 c.c. of this liquid is taken, mixed with phenacetolin, and standard acid added until a pale-rose tint is obtained. In order to estimate both hydroxide and carbonate, the substance is dissolved in standard acid and the excess of acid determined by reverse titration in the usual way (Lunge, *l.c.*).

**Acid carbonate in presence of Normal carbonate.** The *cold* and *dilute* solution of normal carbonate and acid carbonate is mixed with phenol phthalein and standard acid added until the liquid becomes colourless. At this point, which corresponds with the complete conversion of the normal carbonate into acid carbonate, the volume of acid added is read off. The liquid is then boiled and acid is added gradually until the solution remains colourless even after long boiling, and the volume of acid is again read off. If  $x$  represents the first reading, and  $y$  the second reading, then  $2x =$  the normal carbonate, and  $y - 2x =$  the acid carbonate (Warder, A.C.J. 3).

Lunge (S.C.I. 1, 57) proposes a different method based on the reaction—



The solution to be tested is mixed with a measured excess of standard (half normal) ammonia, excess of barium chloride added, and the liquid diluted with recently boiled water to a definite volume. When the precipitate has settled, an aliquot portion of the clear liquid is withdrawn and titrated with standard acid in order to ascertain the excess of ammonia. The difference between the volume of ammonia added and that remaining after precipitation gives the volume

corresponding with the quantity of acid carbonate in the liquid analysed.

**Ammonia.** In order to determine the quantity of free ammonia in a solution of the gas, an accurately measured quantity (10 c.c.) of the liquid is transferred to a light-tared flask and weighed. This gives at once the weight taken for analysis and the sp.gr. The liquid is then titrated with standard acid in the usual way, using litmus, lackmoid, or methyl orange as indicator.

Ammonia in combination is determined by boiling the substance with sodium hydroxide, leading the ammonia into a measured excess of standard acid, and determining the residual acid with standard alkali. The substance is weighed into a flask fitted with a cork, through one hole in which passes a pipette containing a strong solution of sodium hydroxide, whilst through another passes a tube leading to a flask or bulb U-tube containing a known volume of standard acid. The flask or U-tube is fitted with a cork which carries a calcium chloride tube containing beads moistened with some of the acid in order to insure complete absorption of the ammonia. After addition of the sodium hydroxide solution the liquid is gently boiled for half an hour, and the residual acid determined. From the volume of acid which has combined with the ammonia the quantity of the latter is readily calculated.

**Hydrochloric, Hydrobromic, Hydriodic, Sulphuric, Nitric, and Oxalic acids** are readily estimated by direct titration with standard alkali.

**Tartaric, Citric, Acetic, and Lactic acids** can likewise be titrated accurately with standard alkali if phenol phthalein is used as the indicator (Thomson, *l.c.*).

**Boric acid** gives no very definite reaction with the majority of indicators, but it is quite neutral to methyl orange, and hence the quantity of alkali in alkaline borates can be accurately estimated by direct titration with standard acid if methyl orange is used as indicator (Thomson).

**Sulphurous acid** can be titrated directly if methyl orange, phenol phthalein or aurin is used as indicator (Lunge, D.P.J. 250, 530). With methyl orange the hydrogen sulphite  $\text{MHSO}_3$  is the neutral salt, whilst with the other two indicators the normal salt is neutral. This difference can be utilised for the determination of the relative proportions of normal and acid sulphite in the same solution (Blarez, C.R. 103, 69; C. J. Abstracts, 1836, 918). Soda or potash must be used, since ammonia gives inaccurate results.

**Selenious acid** can be titrated with standard barium hydroxide. It is monobasic with methyl orange, and dibasic with phenol phthalein. This difference can be utilised for the estimation of selenious acid in presence of other acids, if the total basicity of the latter is indicated by methyl orange (Blarez, C. R. 103, 804; C. J. Abstracts, 1887, 106).

**Phosphoric and Arsenic acids** are monobasic with methyl orange, and dibasic with phenol phthalein (Joly, C. R. 94, 529; C. J. Abstracts, 1882, 692). These acids can be most accurately titrated with barium hydroxide, using phenol phthalein as indicator. Towards the close of the reaction, time must be allowed for the gelatinous tribarium phosphate to change into

the crystalline dibarium salt (Joly, C. R. 102, 316; C. J. Abstracts, 1886, 418). Advantage can be taken of the different basicity with methyl orange and phenol phthalein to estimate phosphoric acid in presence of monobasic acids such as hydrochloric acid (Joly, C. R. 100, 55; C. J. Abstracts, 1885, 348).

**Carbonic acid** in solution is estimated by adding excess of ammonia and calcium chloride. The liquid is then boiled, and the precipitated calcium carbonate collected, well washed, and dissolved in a measured excess of standard hydrochloric acid, the excess of acid being determined by means of standard alkali, after boiling to expel carbon dioxide. The volume of normal acid actually used  $\times 0.022$  gives the quantity of carbon dioxide.

Insoluble carbonates are weighed into a flask fitted with a cork which carries a bulb and delivery tube. The bulb contains moderately strong hydrochloric acid, which is allowed to drop slowly on the carbonate, and the evolved gas is led into a flask containing strong ammonia solution. This flask is closed with a cork, through which passes the delivery tube, which ends just above the surface of the liquid. The cork also carries an exit tube filled with glass beads moistened with ammonia to arrest the last traces of carbon dioxide. When all the gas has been expelled from the carbonate the ammonia is mixed with calcium chloride, boiled, and the precipitate treated as above. With slight modification this process can be adapted to the estimation of carbon dioxide in aerated waters.

A direct estimation of carbon dioxide by weight is made by placing the substance in a light flask fitted with a cork which carries a bulb containing acid to decompose the carbonate and a tube containing calcium chloride to dry the gas. The apparatus is weighed with the acid in the bulb, &c., after a known weight of carbonate has been introduced. The acid is then allowed to drop on the carbonate, and when decomposition is complete the liquid is boiled for two or three minutes to expel dissolved gas, and a current of air is drawn through the apparatus. The apparatus is again weighed, and the loss of weight gives the amount of carbon dioxide. For various forms of apparatus see Mohr's *Titrirmethode*, Fresenius' *Quantitative Analysis*, or Sutton's *Volumetric Analysis*. When the carbonate is difficult to decompose, it is better to absorb the evolved gas, after drying, in bulbs or tubes containing potash solution or soda lime, the increase in weight giving the amount of carbon dioxide. A very complete form of apparatus for this purpose is described by Classen (Fr. 15, 221). Scheibler's method of estimation by measuring the volume of gas evolved is described in Fresenius' *Quantitative Analysis*, vol. i.

**Combined acids in salts** may be estimated with approximate accuracy by adding to a solution of the salt a measured excess of sodium hydroxide or carbonate. The liquid is boiled, allowed to cool, and diluted to a definite volume. When the precipitate has settled, an aliquot portion of the clear liquid is withdrawn, and the excess of alkali determined by titration. From the volume of alkali used the proportion of acid

in the salt is calculated. In order to avoid the error due to the presence of the precipitate, the liquid may be filtered before diluting to a definite volume, but methyl orange or cochineal must be used as indicator in order to avoid any error from carbon dioxide absorbed from the atmosphere. Salts of copper, silver, mercury, cobalt, nickel, iron, and chromium are precipitated with sodium hydroxide; salts of calcium, barium, strontium, magnesium, aluminium, zinc, bismuth, and manganese, with sodium carbonate.

**Kieffer's method** is useful for coloured solutions, or in presence of normal salts with acid reactions (A. 93, 386). 60 grams of crystallised cupric sulphate is dissolved in water, mixed with ammonia until the precipitate is almost but not quite dissolved, diluted to about 900 c.c., allowed to stand for some time, and the clear liquid siphoned off, or filtered through glass-wool, and diluted to 1000 c.c. If any further precipitate forms it must be siphoned or filtered off. If the solution of cuprammonium sulphate thus obtained is added to an acid liquid, so long as the acid is in excess an ammonium salt and cupric sulphate are formed, but as soon as the free acid is neutralised, the ammonia in a fresh quantity of cuprammonium sulphate reacts on the cupric sulphate already in the liquid and produces a precipitate of a basic salt, the formation of which indicates the point of saturation. The precipitate is most readily seen against a black background. In order to standardise the liquid, 10 c.c. of normal sulphuric acid is placed in a flask or beaker and Kieffer's solution added until a permanent precipitate is produced, and from the volume of solution required, its strength in terms of normal acid is readily calculated. The strength of the solution gradually diminishes, and it must be titrated from time to time. In making an actual determination, the Kieffer's solution is added to the liquid to be tested until a permanent precipitate is formed. The method is not very accurate, owing mainly to the fact that the precipitate is not quite insoluble in solutions of ammonium salts, and therefore the end reaction does not take place until the liquid is saturated with the basic salt. The magnitude of the error depends on the concentration of the solution. When the liquids to be titrated contain barium, strontium, &c., the Kieffer's solution must be prepared with cupric nitrate.

Richter has recommended potassium bichromate as a standard solution for the estimation of alkalis, phenol phthalein being used as indicator (Fr. 21, 205).

Schultze has determined the rates of expansion of standard solutions of acids and alkalis and other solutions employed in volumetric analysis (Fr. 21, 170). The following are the results for average temperatures:—

—	Oxalic Acid	Hydrochloric Acid	Nitric Acid
0°	1000000	1000000	1000000
10°	1000993	1001010	1001800
15°	1001940	1001905	1003050
20°	1003125	1003013	1004490
25°	1004560	1004328	1006120



—	Sulphuric Acid	Potash	Soda
0°	1000000	1000000	1000000
10°	1001720	1001880	1002050
15°	1002945	1003130	1003565
20°	1004385	1004565	1004848
25°	1005990	1006165	1006510

*Bibliography.* — Mohr's *Chemisch-Analytische Titrimethode*, 6th ed. 1886; Sutton's *Volumetric Analysis*, 5th ed.; Fresenius's *Quantitative Chemische Analyse*, V. 2, 6th ed.; Lunge and Hurter's *Alkali-maker's Pocket Book*. C. H. B.

**ACID MAGENTA** *v.* **TRIPHENYLMETHANE COLOURING MATTERS.**

**ACID VIOLET** *v.* **TRIPHENYLMETHANE COLOURING MATTERS.**

**ACID YELLOW** *v.* **AZO-COLOURING MATTERS.**

**ACONITE, ACONITINE** *v.* **VEGETO-ALKALOIDS.**

**ACORUS CALAMUS.** The common sweet flag. The root is used by distillers to flavour gin, and the essential oil by snuff-makers for scenting snuff. It contains a glucoside termed *Acorin*  $C_{36}H_{50}O_6$  (Faust, *Bl.* [2] 9, 392; Thoms, *Ar. Ph.* [3] 24, 465) (*v.* **CALAMUS**).

**ACRIDINE**  $C_{13}H_9N$ . Crude anthracene contains basic substances, and among them acridine, which can be isolated by extracting it with dilute sulphuric acid and adding potassium bichromate to the acid solution. The precipitated acridine chromate is then recrystallised from water, treated with ammonia, and the base crystallised from hot water (Graebe and Caro, *A.* 158, 265; *B.* 13, 99).

Acridine has also been obtained synthetically by passing the vapours of orthotolylaniline and of orthoditolylamine through a tube heated to dull redness (*G.*, *B.* 17, 1370); and by severally heating formic acid and diphenylamine (Bernthsen and Bender, *B.* 16, 767, 1802), chloroform, diphenylamine and zinc oxide (Fischer and Körner, *B.* 17, 101), and aniline and salicylaldehyde (Möhlau, *B.* 19, 2451) with zinc chloride.

*Properties.* — Acridine crystallises in small colourless needles, or four-sided rhombic prisms, sublimes at 100°, melts at 111°, boils above 360° without decomposition, and distils with steam. It is sparingly soluble in hot water, but readily soluble in alcohol, ether and carbon bisulphide, yielding solutions showing a blue fluorescence. When inhaled either as dust or vapour it causes violent sneezing, and in solution both it and its salts cause much irritation on the skin. On treatment with nitric acid it yields two nitro-derivatives (m.p. = 154° and 214°) and a dinitro-derivative (*G.* and *C.*); potassium permanganate oxidises it to *Py.* 2 : 3 quinolinedicarboxylic acid  $C_9H_5N(CO_2H)_2$ , and sodium amalgam reduces it to *hydroacridine*  $C_9H_9N$  (*B.* and *B.* 16, 1971; *G.*, *B.* 16, 2831). The salts are yellow and crystallise well, but are decomposed into their constituents on boiling.

*Methylacridine*  $C_{11}H_9N$  is obtained by heating diphenylamine and acetic acid with zinc chloride (Besthorn and Fischer, *B.* 16, 74; compare Fischer, *B.* 16, 1820), and crystallises in colourless tabular crystals melting at 114°.

*Phenylacridine*  $C_{19}H_{13}N$  is obtained by heating diphenylamine with benzoic acid and zinc

chloride at 260° (Bernthsen, *B.* 15, 3012; 16, 767, 1810), and melts at 181°.

**ADAMANTINE SPAR** *v.* **CORUNDUM.**

**ADAMINE.** A hydrated zinc arsenate from Chanarcillo, Chili, containing 39.85 p.c.  $As_2O_3$ , 54.32 ZnO, 1.48 FeO, trace MnO and 4.55 water. Its sp.gr. is 4.338 (Friedel, *Bl.* [2] 5, 433).

**ADANSONIA DIGITATA**, the *Baobab tree*, yields a fibre which has been used in paper-making. Its bark (Gowik Chentz or Churee Chentz) is said by Duchassaing to be a useful substitute for cinchona (Dymock, *Ph.* [3] 7, 3).

**ADIPIC ACIDS**  $C_6H_{10}O_4$ . The fifth term of the oxalic acid series having the general formula  $C_nH_{2n-2}O_4$ . There are nine possible adipic acids, all of which, with the possible exception of one, have been prepared. Ordinary adipic acid is produced by the action of nitric acid on tallow, suet, and other fatty bodies. Adipic acid crystallises in monoclinic laminæ, melts at 149°, and sublimes at a still higher temperature (Wirz, *A.* 104, 257). By destructive distillation, especially with lime, it yields butane and carbon dioxide,  $C_6H_{10}O_4 = C_4H_{10} + 2CO_2$ . It is slightly soluble in water at the ordinary temperature, and has a great tendency to form supersaturated solutions (Dieterle and Hell, *B.* 17, 2221); readily soluble in hot alcohol and ether. It forms salts with most metals, which are generally soluble in water and crystallisable.

For isomerides of adipic acid, *v.* **WATTS' DICTIONARY OF CHEMISTRY**, vol. i. p. 63.

**ADIPOCERE** (from *adeps*, fat; and *cera*, wax). A peculiar waxy-looking substance, formed by the decomposition of animal matter from which the air has been excluded. It was first observed by Fourcroy in 1786, when the *Cimetière des Innocens* at Paris was cleaned out. A large number of coffins had been piled together and had remained for many years; the corpses in many of these were converted into a saponaceous white substance. According to Ebert (*B.* 8, 775) adipocere consists chiefly of a mixture of fatty acids, glycerine being absent. On saponifying with potash, about 1 p.c. ammonia escapes and an insoluble residue (about 6 p.c.), consisting of lime, &c., from tissues, remains. A mixture of potassium salts was obtained, which by fractional precipitation with magnesium acetate yielded mainly palmitic acid, also a small quantity of margaric acid, hitherto only formed synthetically. The last fraction, not precipitable by magnesium, but by lead acetate, gave oxymargaric acid ( $C_{17}H_{31}O_2$ ). Oleic acid was not present.

Of late years the formation of adipocere from animal matter has been studied in glass vessels filled with water (Kratter). It is not a decomposition product of albuminous tissue (Erman), but is formed from the various fats present in the body at the moment of death (Zillner), the fatty matter collecting together, after some time undergoing further decomposition, eventually losing its glycerol and oleic acid (Zillner).

**AERATED WATERS.** The names 'aerated' or 'mineral' waters are applied to water charged with an abnormal quantity of gas, usually carbon dioxide. Water in this condition exists in natural springs in various places, as at Vichy, Spa, Seltz; or it may be produced by artificial means. The natural springs vary in character from the

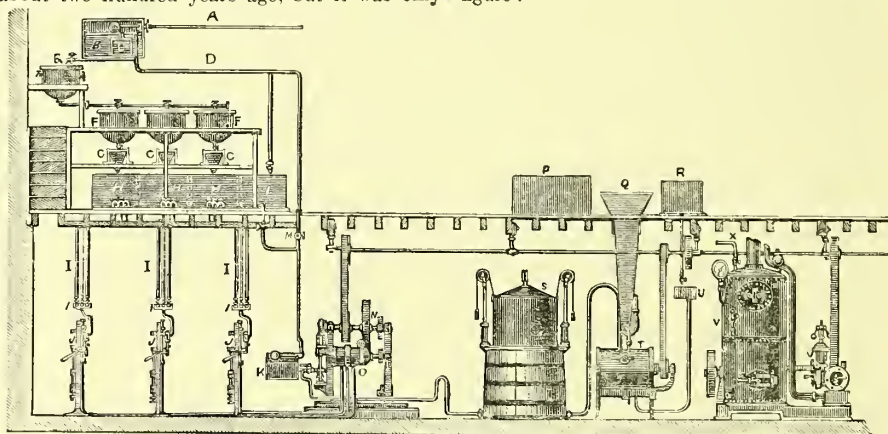


fact that along with the gas, which gives more or less effervescence to their waters, other ingredients enter, giving to each locality its claim to specific medicinal efficacy. These waters being also pleasant and refreshing to the taste are esteemed as beverages alone. Among artificially produced quasi-mineral waters, a common form is that of the Seidlitz, prepared from sodium bicarbonate and tartaric acid, which are kept separate until required for use; on the addition of water, proportioned to the quantity of powder, the acid reacts on the bicarbonate, and a lively effervescence is set up by the liberated carbonic acid gas. Numerous modifications of the seidlitz powder have been introduced for public sale under special designations; they usually consist of the same ingredients, with the addition of a little citric acid.

The attempt to imitate natural medicinal spring-waters appears to have been made about two hundred years ago, but it was only

towards the close of the last century that the manufacture began to assume anything like commercial importance. Within the last few years much attention has been paid by inventors to the cheap and expeditious manufacture of artificial mineral waters and aerated beverages, and to the bottling and other processes; so much so that the applications for Letters Patent under the title 'Aerated liquids; mineral waters; aerating,' more or less applicable to the heading of this article, were—in 1882, five; in 1883, three; in 1884, twenty-one; in 1885, thirty-five; and in 1886, thirty-one. 'Bottle and jar stoppers,' for the most part applicable to aerated waters, in 1886 claim 184 inventors; and 'Bottle-opening and unstoppering,' twenty-five. Manufactories of these drinks are now found in almost every town in the kingdom.

The general arrangement of the apparatus employed will be made clear from the following figure:—



PLAN OF A SODA-WATER MANUFACTORY.

- A. Main water-supply from well or waterworks.
- B. Water reserve.
- C. Filter.
- D. Pipe and branches supplying filtered water to syrup-boiler, solution-tank, and soda-water machine.
- E. Steam-cased pan for boiling syrups.
- FFF. Mixing and cooling-pans for syrups.
- GGG. Felt filtering-bags, through which syrup is passed.
- HHH. Tank in compartments for storing filtered syrups.
- III. Syrup junctions and pipes supplying syrup pumps at bottling-machines.
- JJJ. Bottling-machines.
- K. Solution-pan feeding soda-water machine with either plain water from filter C, or soda or other solution from tank L.
- L. Soda-water solution tank for mixing mineral waters

- which require no syrup. When using this tank the tap M is closed.
- M. Tap to shut off plain filtered water when bottling non-saccharine beverages.
- N. Soda-water machine.
- O. Condenser containing aerated water, to which pipes leading to bottling machines are attached.
- P. Whiting bin.
- Q. Whiting shoot to generator.
- R. Vitriol cistern.
- S. Gasometer.
- T. Generator.
- U. Blow-back prevention acid box.
- V. Steam-engine.
- X. Steam-pipe to syrup boiler and bottle-washing apparatus.

In reference to E and X, when gas-engines are used as the motive-power, and no steam is available for boiling syrup, it is usual to employ an apparatus heated by gas.

It will be noted that the plant here figured is adapted to produce (1) water simply charged under pressure with gas; or (2) alkaline, or (3) sweetened effervescing drinks, and that any of these can be made at the will of the operator. In all cases carbonic acid gas is evolved in the generator by the mixture of sulphuric acid with chalk or whiting, is stored in the gasometer, is conveyed to the condenser along with water from the cistern, and, after solution, is thence drawn to the bottling ma-

chines. The pressure in the condenser is indicated by a gauge, and varies with the beverages made; thus, for soda-water a pressure of 120 lbs. to 140 lbs. per sq. in. is required, whilst for sweetened beverages 80 lbs. to 100 lbs. is sufficient.

The generator is ordinarily of lead, and is either vertical or, preferably, horizontal, and is fitted with an agitator of gun-metal or of copper, to mix thoroughly the carbonate of lime and acid. Besides two openings to admit these materials, it has a third for the purpose of their removal when exhausted. The gas-holder is simple in construction, the well or tank being made of oak well-hooped, and the rising-bell of

stout sheet-copper, tinned within and without. To prevent the bell from collapsing when the machine is working and the gas is exhausted, it is often fitted with a valve.

Although not absolutely necessary, it is advisable to use a gas-purifier in preference to allowing the gas to be pumped direct from the gas-holder. The purifier is simply a vessel containing water through which the gas passes. The soda-water machine consists of one, or, in large machines, two pumps which simultaneously draw the gas from the gas-holder and the water from the cistern: these are forced into the cylinder or condenser, of which there may be one or two constructed of gun-metal, tinned inside and fitted with water-gauge, pressure-gauge, and safety-valve. These cylinders are tested in large machines to as much as 500 lbs. pressure to the square inch. By an ingenious arrangement, called a blow-back escape safety-valve, the excess of gas may be taken back instead of being blown away, thus enabling the largest machines capable of occupying several bottlers to be so regulated that one man may be kept comfortably at work without the machine unduly gaining on him. Such a machine having two 2½-inch pumps, 6-inch stroke, with two 6-gallon cylinders will keep four bottlers at work, each going at the rate of forty dozen per hour: whilst one having two 3-inch pumps, 7-inch stroke, and two 12-gallon cylinders will employ eight bottlers at the same rate.

Beverages flavoured with fruit essences or syrups, such as lemonade, are produced by the admixture in regulated quantities of such syrups with the aerated water, by means of the pumps shown in the figure. Of these flavouring compounds a very large number are used under different names, such as, oil of lemon, essences of lemon, ginger, capsicum, horehound, pear, vanilla, orange, raspberry, cloves and various other fruits and spices.

The tank L is employed when saline and other solutions are required, which for the most part are imitations of the waters of well-known natural mineral springs, or are approved medicinal combinations.

The minor appliances of the industry, such as bottle-washing machines, bottling machines and their accessories, are endless in number and variety, as may be seen by a reference to the specifications of patents. A determined effort has been made, and with great success, to supersede corks in stoppering bottles containing these liquids, on account, partly, of convenience to the consumer, but chiefly on account of economy. In an estimate of the total cost of the materials used in making a certain quantity of soda-water, amounting to 11l. 4s. 4d., no less than 7l. 10s. 0d. is set down to the account of corks. Consequently a method of bottling has been adopted wherein the neck of the bottle is closed by the pressure of the gas within it holding a marble of glass, plugs of wood, or other stoppers firmly in the mouth, which is necessarily smaller than the marble or plug. When it is required to open the bottle, the stopper is pushed down; whereupon the contents are liberated. By these and similar contrivances, the cost of producing these beverages has been greatly reduced; and probably from this cause, as well as from a change in the

public taste, the consumption of them has greatly increased during recent years.

**ÆRUGO.** (*Verdigris* (?) or basic carbonate of copper.) The name given by the Romans to the green rust produced on copper and bronze by the united action of the oxygen and carbon dioxide of the air. It was considered by them to enhance the beauty of their bronze statues. The same rust forms on brass, which was, however, not used by the Romans.

**ÆSCULIN** v. **GLUCOSIDES.**

**AFRICAN ELEM** v. **OLEO-RESINS.**

**AFRICAN FISH OIL.** An oil of unknown constitution, sp.gr. 0·865 to 0·867. It will not saponify (Allen, S. C. I. 2, 54).

**AFRICAN GREEN** or **EMERALD GREEN** v. **PIGMENTS.**

**AFRICAN INCENSE** v. **OLEO-RESINS.**

**AGALITE.** A fibrous magnesian silicate of a white colour, with a slight tinge of green; found in America. It is somewhat readily reduced to a powder, the particles composing which are fibrous. Used in paper-making to impart a beautiful surface and gloss to the paper (Macadam, S. C. I. 6, 126).

**AGAR-AGAR.** Bengal Isinglass. A dried seaweed obtained from Singapore. Consists of *Eucheuma spinosum*; *Sphaerococcus lichnoides*, *spinosus* and *tenax*.

It occurs in small, transparent strips, and dissolves almost entirely in water to a gelatinous, tasteless and inodorous jelly, v. **ALGÆ.**

**AGATE.** (*Achat*, Ger.) A natural aggregate of various forms of crystalline, crypto-crystalline and colloidal silica. In most agates these siliceous minerals are arranged in alternating layers, which present on section a banded appearance, whence the agate is valued, when cut and polished, as an ornamental stone. This zoned structure is usually the result of the deposition of silica in successive layers within the cavities of a vesicular rock. In some cases, however, the deposition has been effected in fissures, thus forming siliceous veins, as in the brecciated agates of Saxony and Bohemia. In other cases the agates may occur in the cavities of stratified rocks, or occupy the spaces between the pebbles of a conglomerate: such are the agates of the dolomitic conglomerate and the 'potato stones' of the Triassic marls of Somersetshire (Trans. Geol. Soc., ser. II. vol. iii. p. 421). Rupert Jones has suggested that in many cases these agates have been formed by the replacement of  $\text{CaCO}_3$  by  $\text{SiO}_2$  (Proc. Geol. Assoc. IV, 1876, p. 454).

The artificial deposition of silica, in forms closely resembling those of certain agates, has been effected by TAnson and Pankhurst (Min. Mag. v. 1882, p. 34). A strong acid is introduced by means of a pipette into a solution of an alkaline silicate, containing a certain proportion of alkaline carbonate; the bubbles of carbon dioxide set free become coated as they ascend with gelatinous silica, which forms a tube; and by continued deposition a stalactiform agate is produced. If a cavity in a rock were filled with a solution of an alkaline silicate, and the rock permeated by an acid, a layer of amorphous hydrated silica would be deposited upon the walls of the cavity, and through this gelatinous layer further deposition might gradually proceed.

The rocks in which agates typically occur are the basic igneous rocks known as basalt, dolerite, diabase and melaphyre. These 'traps' are essentially plagioclase-augite rocks. In many cases they present a vesicular texture, and the vesicles may inclose various secondary minerals resulting from the decomposition of the constituents of the rock. Among the commonest of these alteration-products is the green earthy mineral known as *delessite*, a hydrated silicate of aluminium, iron, and magnesium, probably a product of the decomposition of the augite. Many vesicles are simply lined with this green substance, but in other cases the *delessite* becomes covered by subsequent mineral-deposits until the cavities are more or less completely filled. The rock thus becomes 'amygdaloidal,' a term suggested by the fact that the kernels of mineral are usually of almond-like shape. This shape is due to the cavities, which were originally gas- or steam-bubbles, having been elongated by the flow of the lava-like rock when viscous. In many cases the 'amygdules,' or contents of the cavities, are kernels of calcite, but in other cases they are siliceous. If hollow they form *geodes*; and when nearly filled with alternate layers of chalcedony, jasper, quartz and other forms of silica, they constitute true agates.

The embedded agates are easily detached from the inclosing rock, and when removed usually present a pitted surface. On the exterior is a green coating or 'skin' of *delessite*, or of the similar mineral chlorophæite: many of the larger agates, however, present a rusty coating of ferric hydrate. The earliest-formed siliceous deposits are usually chalcedonic, and the latest are often crystalline: thus in a hollow agate the interior is generally lined with a crop of quartz crystals, not unfrequently amethystine, the apices of the pyramidal crystals being directed towards the central cavity. This structure shows that the agate has been formed by successive deposition from without inwards: in other words, the growth has been 'endogenous.' It is notable that in certain agates the first-formed layers have been concentric with the walls of the original cavity, and the subsequent strata horizontal.

Tubular orifices, lined with siliceous deposits, may be detected in many agates, and these have been commonly regarded as inlets of infiltration, or channels through which the siliceous solution gained access to the interior. It has, however, been held by many observers that the solution, so far from having been introduced through a definite aperture, gradually filtered in at all points; and the internal walls thus became uniformly coated with a gelatinous layer, which allowed the further introduction of silica by osmotic action. Dr. Heddle has pointed out that if, by a difference in the density of the siliceous solutions within and without the cavity, pressure were exerted outwards against the gelatinous medium, this deposit might give way, and the so-called inlet would thus be really a point of egress (N. xxix. 1884, p. 419). E. Reusch has suggested that the agate bearing cavities were filled periodically with hot siliceous solutions by the action of intermittent thermal springs (P. exxiii. 1864, p. 94). G. Lange, extending this view, supposes that the steam from the solution confined in the cavity might exert suffi-

cient pressure outwards to pierce the gelatinous deposit, and thus an outlet of escape might be mistaken for an inlet of infiltration. Possibly it sometimes happens, as maintained by Bischof (Chem. Geol., Auf. II. 1866, III. p. 621), that the cavities in which agates occur, instead of having been originally vesicles in an eruptive rock, were hollows left by the removal of crystals in a rock of porphyritic texture; but such an explanation does not admit of general application.

Agates, when released from their matrix by its natural disintegration, occur as loose nodules, either in the beds of rivers or scattered over the country in pebble-drifts. The 'Scotch pebbles' are found chiefly near Montrose in Forfarshire, and at the Hill of Kinnoul in Perthshire. The agates of the Cheviots are found in the Coquet and other Northumbrian rivers. In India agates have for ages been worked by the lapidaries of Cambay, Broach and Ratanpur, who obtain their supply from the traps of the Deccan and of the Rájmahál Hills, or from the agate-bearing gravels of Rajpipla, which are systematically mined (Man. Geol. India, pt. III. [V. Ball], 1881, p. 503; pt. IV. [F. R. Mallet], 1887, p. 70). In S. Africa agate-pebbles occur in the Orange and Vaal Rivers. In the U.S. the localities are numerous—e.g. the shores of L. Superior, the Pescadero beach in California, along the Connecticut River, the Mississippi, the Fox R., Illinois, and the Yellowstone National Park (G. F. Kunz, in Min. Resources of U.S., 1885, pp. 756, 757). In Queensland is a locality known as Agate Creek, running into the Gilbert R. (For New South Wales, see A. Liversidge, Min. of N.S.W., 1888, p. 169.)

The largest and finest agates are the so-called Brazilian stones, which come chiefly from Uruguay, where they occur as pebbles in the beds of rivers, especially the R. Taquarie, having been derived from amygdaloidal trap rocks. Of late years some interesting agates have been obtained from this country, consisting of a rind of chalcedony, lined with quartz crystals and containing liquid, moveable within. These have been called *water-stones*, *hydrolites* or *enhydros*. According to C. W. Gumbel the liquid is water with a small quantity of NaCl, CaCl<sub>2</sub>, CaSO<sub>4</sub>, SiO<sub>2</sub>, CO<sub>2</sub>, &c. (Sitz. B. z. München, 1880, II. p. 241; 1881, III. p. 321). Chalcedonic waterstones, of polyhedral form, occur at Beechworth, Victoria.

Moss agate consists of chalcedony inclosing twisted filaments, usually green but sometimes red or brown, resembling vegetable structures. In most cases they are certainly merely mineral inclosures, but some forms have been regarded as organic (Macculloch, Trans. Geol. Soc. ii. p. 510). *Mocha stones* are simply white or brown chalcedony, generally from India, with dendritic or arborescent markings due to oxides of iron and manganese. *Fortification agate* is a term applied to those stones in which strata of jasper and chalcedony have been deposited upon quartz crystals, and hence they present on section curious zig-zag patterns, suggestive of the plan of a fortress. The trivial terms *eye agate*, *riband agate*, &c., need no explanation.

Agate is employed for the knife-edges of balances, for small mortars and pestles, for burnishers and writing styles, for trinket-boxes, umbrella-handles, seals, brooches, beads and an



endless variety of trivial ornaments. Nearly all the agate used in the arts is worked in Germany.

The industry of cutting and polishing agates is centred in the neighbourhood of Oberstein on the river Nahe, a tributary to the Rhine at Bingen. Most of the agate mills are situated near Idar, about two miles north of Oberstein. Here the Idar Bach, which flows into the Nahe, furnishes abundant water-power, which for four centuries has been utilised in the local mills. The original location of the trade in this district was due to the occurrence of agates in the amygdaloidal melaphyre of the Galgenberg, near Idar, where agates were formerly obtained by systematic mining operations. For many years, however, these workings have been abandoned, and the mills have been supplied with South American agates, the importation of which was begun about 1827.

Large consignments of agates are periodically sold by auction at Oberstein. The common stones are first roughly dressed with hammer and chisel, while the finer stones are carefully wrought into form by means of metal discs fed with emery or with diamond powder. The grinding is performed on wheels of red sandstone, about 5 feet in diameter, set vertically, and rotating at the rate of about three revolutions per second. Each stone is about one foot in width, and its surface presents channels corresponding with the form of the objects to be ground. The stones are usually moved by large undershot water-wheels, but the inconvenience of their stoppage during the drought of summer or the frost of winter has led to the partial introduction of steam-power. When working, the grinder lies almost horizontally upon a wooden stool, hollowed to the shape of his body, and having his arms free. The agate is pressed forcibly against the grindstone, fed with water from above, while the workman obtains purchase by pressing his feet against a block fastened to the floor. The polishing is afterwards effected with rouge and water on soft metal plates or with tripoli on wooden cylinders.

Not only agates, but rock-crystal, amethyst, false crocidolite, and other hard stones are now extensively cut and polished by the Idar lapidaries. These stones are also cut, to a limited extent, at Waldkirch in the Black Forest (Groth, *Edelsteinkunde*, 1887, p. 155).

For many years the German agate-workers, following the earlier practice of the Italian cameo-cutters, have modified the colour of most of the stones by staining them. The commonest practice is that of darkening certain layers in a banded agate, so as to produce an *onyx*. The *onyx* presents a succession of two or more strata, alternately light and dark brown, or even white and black. To produce this contrast of colour when not naturally present, the agate is first steeped in honey and water, and gently heated on a stove. In course of time, perhaps two or three weeks, certain layers of chalcedony, more porous than others, are found to have absorbed the saccharine matter. No perceptible change is observed when the agate is removed and washed; but on placing it for a short time in sulphuric acid the absorbed matter becomes carbonised, and it is then seen that certain layers of chalcedony, originally of a dull grey

tint, have assumed a rich brown or even black colour. In place of the honey, olive oil is sometimes used. If accidentally coloured too strong, the excess may be removed, or the colour 'drawn,' by the use of nitric acid. The process of darkening agates is one of great antiquity, and is imperfectly described by Pliny (*Hist. Nat.* xxxvii. c. 75) as having been in his day practised in Arabia. On the history of colouring agates, v. Nöggerath, *Die Kunst, Onyxen . . . zu färben*, *Karsten's Archiv*, xxii, 1848, p. 262.

*Carnelian* is a red variety of chalcedony, and its characteristic tint may be easily developed artificially in the chalcedonic bands of certain agates which are, in their natural state, merely grey or yellowish. It has long been the practice in India to heighten the colour of pale brownish agates by prolonged exposure to solar heat, whereby any ferric hydrate in the stone loses more or less water. In Germany the agate is usually heated and then moistened with sulphuric acid, or is placed in a solution of ferric nitrate, crudely prepared by throwing old nails into dilute aquafortis; in either case the stone is afterwards exposed to a red heat, whereby the absorbed salt is decomposed and ferric oxide formed. Alternating bands of red and white chalcedony constitute the variety of agate known as *sardonyx*, and it is to imitate this stone that the red tints are often developed. Prolonged digestion in warm hydrochloric acid imparts a yellow tint to the agate, but this colour is not popular. Green colours, resembling those of *chrysoprase*, which is simply a green chalcedony, are produced by means of salts of either nickel or chromium. Blue tints may be readily obtained by soaking the stone in a solution of ferrous sulphate and afterwards in either ferrocyanide or ferricyanide of potassium, when Prussian blue or Turnbull's blue is thrown down in the pores of the stone; or an ammoniacal solution of sulphate of copper may be used. Blue agates, artificially stained, are extensively sold as lapis lazuli. Quite recently a dead-white effect has been produced in certain stones, which are thus rendered more valuable for cameo work. It is said that this effect is obtained by the use of caustic potash and subsequent exposure to a high temperature. On the agate industry, v. H. Lange, *Die Halbedelsteine*, Kreuznach, 1868; and Uppmann, *Beitr. z. Gesch. d. Gräfsch. Oberstein*, Mainz, 1872.

F. W. R.

**AGONIADA BARK.** The bark of *Plumeria longifolia*, used in Brazil as a remedy for intermittent fever, contains a bitter crystalline substance, *agoniadin*, having the composition  $C_{16}H_{11}O_6$  (Peckolt, *Ar. Ph.* [2] 144, 34).

**AGRICOLITE or AHELESTITE.** A mineral found at Schneeberg in Saxony containing 57.15 p.c.  $Bi_2O_3$ ; 12.50  $Fe_2O_3$ ; and 30.35  $As_2O_3$  (Frenzel, *J. M.* 1873, 785).

**AICH METAL.** An alloy patented by J. Aich in 1860 for use as sheathing for ships. Contains copper, 60 parts; zinc, 38.5 parts; iron, 1.5 part.

**AILANTHUS BARK.** The inner bark of *A. excelsa* and *A. glandulosa*; it has the odour and taste of cinnamon; used as a tonic in dyspepsia (Dymock, *Ph.* [3] 7, 309). Its Indian name is *Maharook*.

**AKANDA v. AK MUDAR.**



**AK MUDAR, AKANDA, AKRA RUI, or ERUKKU ERUKKAM.** The bark of *Calotropis gigantea* and *C. procera*. An important Indian drug (Dymock, Ph. [3] 10, 122).

**AKOLA** *v.* ANKOOL.

**AKRA RUI** *v.* AK MUDAR.

**ALABAMITE**, *Manganese sulphide*, *v.* MANGANESE.

**ALABASTER.** (*Albâtre*, Fr.; *Alabaster*, Ger.) A crystalline calcium sulphate found massive in Glamorganshire; at Syston, in Leicestershire; at Tutbury, near Burton-on-Trent, in Staffordshire, and other places in Britain. A snow-white alabaster much used for small ornamental objects, such as vases, lamps, stands of time-pieces, &c., is found at Volterra, in Tuscany. The harder varieties are worked with the same tools as marble, smoothed with pumice stone, polished with a mixture of chalk, soap, and milk, and finished by friction with a flannel.

The softer kinds may be turned or fashioned with rasping tools, file chisels or small files, smoothed with dried slave grass, then rubbed with a paste of putty powder or finely divided slaked lime, and polished by washing with soap, water and lime, and finally with powdered elutriated French chalk or tale.

Alabaster may be stained by heating it to about 90° or 100° C., and then dipping it into the colouring solution which may be either metallic solutions, spirituous tinctures of dyeing plants, or coloured oils (Habild, W. J. 28, 669).

A variety of alabaster known as Onyx of Tecali, from Mexico, takes a fine polish; its colour varies from milk-white to pale-yellow and pale-green (J. 29, 1264).

**ALANGIUM LAMARCKII** *v.* ANKOOL.

**ALANT CAMPHOR** *v.* CAMPHOR.

**ALASKAITE.** A mineral found in the Alaska Mine, Ouray Co., Colorado, containing:—

	Bi.	Pb.	Ag.	Cu.	Zn.	Fe.	S.	Insol. Sb.
<i>a</i>	51.49	12.02	8.08	3.00	0.26	—	15.72	—
<i>b</i>	46.87	9.70	7.10	2.85	0.64	—	15.07	0.51
<i>c</i>	51.35	17.51	3.00	3.74	0.20	—	16.21	—
<i>d</i>	53.39	12.02	7.80	5.11	0.34	0.84	17.98	1.80

(König, *a-c*, J. M. 1883, 1. R. 25; *d*, Zeit. Kryst. Min. 11, 290; C. J. [2] 44, 429; 50, 515.)

**ALBERTITE.** A jet-black mineral substance, resembling asphalt, discovered in 1849, at Hillsborough, Albert Co., New Brunswick. Is largely used in the United States for the distillation of oil and coke. Theyield per ton is said to be 100 gallons of crude oil, and 14,500 cubic feet of illuminating gas, while a residue of good coke remains in the retorts. Albertite has been found at Strathpeffer, Ross-shire; it contains 62 p.c. volatile matter, 37 p.c. fixed carbon, and 0.60 p.c. water. Its ultimate composition is 79.75 p.c. carbon, 8.12 p.c. hydrogen, 1.63 nitrogen, and 10.30 oxygen (Morrison, Min. Mag. 6, 101; C. J. [2] 50, 311).

**ALBU-LIGNOSINE** is prepared by boiling wood or other fibrous substances under pressure in a solution of sodium sulphite; acidifying the solution and adding albumen. Used as a size, mordant, and vehicle for colours and pigments (Cross and Bevan, Eng. pat. 1548, 1883; S. C. I 2, 541).

**ALBUM GRÆCUM.** A term formerly used for the excrement of dogs. It was at one time supposed to have medicinal properties, but is

now used only for tanning, as skins treated with it, after the removal of the hair and previous to tanning, preserve their softness. Fowls' dung is said by tanners to answer the purpose better. It consists mainly of phosphate of lime.

**ALBUMINOIDS.** The albuminoids are a class of carbon compounds of a very complex nature, whose properties comply more or less closely with those enumerated in a subsequent paragraph. They only occur in nature, in plants and animals, and are essential to both forms of life; the group also includes certain substances produced by the action of reagents on these plant and animal albuminoids, but no albuminoid has yet been prepared artificially from non-albuminoid substances. It is noteworthy that it is only plant life that can synthesise an albuminoid from other forms of matter and that the animal is dependent on plant life for the albuminoids necessary for its existence; the animal can, however, transform one albuminoid into another or into a substance of the allied gelatinoid and keratin groups; besides being able to effect its conversion into fat or into simpler oxidation products. The greater part of the nitrogen of the albuminoids oxidised in the body is excreted by the kidneys as urea; the urea thus excreted is approximately one-third of the weight of the albuminoids oxidised. The name 'Albuminoid' is given to them from their similarity to albumin, a member of the group occurring in white of egg (Latin, *albumen*). An alternative name for the group is 'the proteids' from protein (*πρωτεῖος*, 'holding the first place') a name given by Mulder to a substance which, he supposed, when combined with sulphur, phosphorus, &c., formed the albuminoids; his views, however, turned out to be incorrect.

*General Properties.*—All albuminoids contain the five elements, carbon, hydrogen, oxygen, nitrogen, and sulphur. They do not differ much from one another in their percentage composition; the percentages found varying within fairly narrow limits, viz.:—carbon, 50–55; hydrogen, 6.9–7.5; oxygen, 20–24; nitrogen, 15–18; sulphur, 3–2.0. They usually leave some ash when incinerated, and this ash contains phosphates and other salts. When heated in solution or in suspension, many of them undergo a change known as coagulation, *i.e.* they are changed into substances which are insoluble in the weak solvents: water, saline solutions, dilute acids, and dilute alkalis; this change commences in some cases at 60° or even lower. With the exception of the peptones, the albuminoids diffuse through a membrane extremely slowly. Alcohol in large excess; nitric acid enough to make the solution strongly acid; acetic acid and potassium ferrocyanide; basic lead acetate; mercuric chloride; potassium platino-cyanide; potassio-mercuric iodide in presence of free hydrochloric acid; are reagents that effect the precipitation of many of the albuminoids from their solutions. One of the best tests for detecting the presence of albuminoids is Millon's reagent. This is prepared by treating mercury with its own weight of nitric acid of specific gravity 1.4; when the action slackens, gentle heat is applied until all the mercury is dissolved; the solution is then diluted with twice its volume of water and

allowed to stand for some hours, a deposit separates, and the liquid decanted off from this is Millon's reagent. Albuminoids, both solid and in solution, boiled with this reagent give a red colour, and the liquid also becomes red, but some time must be allowed. It must be remembered that members of the allied gelatinoid and keratin groups and silk also give the red colour.

Several of them (and gelatin as well) change the blue colour of sugar test (potassio-cupric tartrate in solution with potassium hydroxide) to a violet colour resembling that of potassium permanganate.

Boiled for some time with concentrated nitric acid, solutions of the albuminoids give a yellow colour which changes to orange on the addition of ammonia in excess. This is known as the xantho-proteic reaction.

All the albuminoids when in solution are levorotary in their action on polarised light, and a determination of this power is of great importance for purposes of identification.

The chemistry of the albuminoids as definite compounds is scarcely yet known, and very conflicting views have been entertained about the identity of many members of the group. Béchamp (Mem. sur Albd. 1884) has made very exhaustive researches on the albuminoids, taking great precautions to separate one albuminoid from another, by the employment of various solvents, precipitants, and fractional precipitation, and using the polariscope to identify the substances obtained. He holds that attempts have been too much directed to prove the identity of albuminoids from different sources; whereas his methods lead to the conclusion that the number of different albuminoids is considerably greater than is now admitted, and that many of the albuminoids at present described are in reality mixtures. A consideration of the large number of compounds that occur in the carbohydrate group, whose composition is far simpler than that of the albuminoids, renders this view very probable, and Béchamp's work may lead to a revision of the albuminoids.

**Classification.**—The albuminoids are classified into seven groups.

I. *The Albumins.*—These are soluble in water, in neutral saline solutions, in dilute acids and dilute alkalis, and are colloids.

Egg albumin.	Crystallin.
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Serum albumin.	
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II. *The Globulins.*—These are insoluble in water, but are soluble in neutral saline solutions, in dilute acids and dilute alkalis.

Myosin.	Fibrinogen.
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Serum globulin.	Vitellin.
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III. *Derived Albumins.*—These are insoluble in water and in neutral saline solutions, but are soluble in dilute acids and dilute alkalis.

Acid albumin.	Alkali albumin.
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Syntonin.	Casein.
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IV. *Fibrin*, which is insoluble in water, and is soluble, with difficulty, in neutral saline solutions and in dilute acids and dilute alkalis.

V. *Coagulated Albuminoids.*—These are insoluble in water, neutral saline solutions, dilute acids, and dilute alkalis. They are the substances produced by the action of heat or of strong alcohol on many of the albuminoids when in solution or in suspension in water.

They are attacked by strong acids and alkalis, and can be converted into peptones by artificial gastric or pancreatic juice.

VI. *Lardacéin* or *Amyloid* is an albuminoid substance occurring in diseased liver, spleen, &c. It is insoluble in water and in dilute acids, but is soluble in moderately dilute ammonia. Its most characteristic features are that it is not converted into a peptone by artificial gastric juice, and that with strong sulphuric acid and iodine it is coloured violet or blue.

VII. *The Peptones.*—These are soluble in water, neutral saline solutions, dilute acids and dilute alkalis; they differ from the albumins in being diffusible through membranes, and in that their solutions are not coagulated by heat. They are produced by the action of the gastric and pancreatic juices on the albuminoids.

The vegetable albuminoids are numerous, but they have not been so much studied as the animal albuminoids, and gluten is the only substance that will be described.

#### *The Albumins.*

##### **Egg Albumin.**

**Occurrence.**—It forms the chief part of the organic substance of the white of birds' eggs.

**Preparation.**—1. White of egg is cut up with scissors, squeezed through linen, filtered without access of air, diluted with much water, and to the liquid acetic acid is carefully added to precipitate a few floccs of some albuminoid substance. After filtration the liquid is dialysed to remove salts as far as possible.—2. After diluting and filtering the white of egg, basic acetate of lead is added, but not in excess, as that would dissolve the precipitate formed. This precipitate is suspended in water, and the lead is removed by a current of carbon dioxide; the last traces being got rid of by adding a little hydrosulphuric acid, and heating enough to coagulate a little albumin, which carries down the lead sulphide with it. After filtration the liquid is evaporated at 50°. The albumin thus obtained is only one of the ingredients of white of egg (*v. Proximate composition*).—3. For technological purposes, white of egg is evaporated to dryness in the air at moderate temperatures, and the resulting light-yellow horny flakes form the commercial egg albumin.

**Properties of dried albumin.**—Dried albumin forms a white or pale-yellow translucent mass, which is hard and brittle and can be easily triturated to a white powder. It is tasteless and inodorous. It is soluble in water but does not dissolve freely; it dissolves readily, however, if the water contain an alkaline salt. It may be heated to 100° without becoming insoluble in water; at 140° it loses 4 p.c. of water but still retains its solubility.

**Properties of an aqueous solution of albumin.** When the solution is beaten it becomes opaline at 60°, and between 60° and 75° the albumin changes into a white insoluble substance known as coagulated albumin. The solution has a rotary power of  $(\alpha)_D = -38^\circ$  (Haas).

Soluble albumin is neutral to vegetable colours.

Albumin is insoluble in alcohol and in ether. Strong alcohol added in large excess precipitates albumin in the coagulated state, but a small quantity of weak alcohol produces a precipitate



which is completely soluble in water. Ether shaken up with a solution of albumin of moderate strength coagulates only a small portion of it.

Nitric acid produces a precipitate and is used as a test for the presence of soluble albumin; warming aids the precipitation.

Dilute sulphuric acid produces a precipitate only after some time. A small quantity of hydrochloric acid produces no precipitate, but a large quantity throws down a substance which contains hydrochloric acid. Metaphosphoric acid, or a solution of a metaphosphate and acetic acid, produces a precipitate. Pyrophosphoric acid, orthophosphoric acid, acetic acid and carbonic acid do not give precipitates. Dilute solutions of potassium and sodium hydroxides do not produce precipitates. Acids and alkalis produce a change in the properties of albumin which will be described under the heads of *Acid Albumin* and *Alkali Albumin*.

Solutions of sodium chloride and other similar salts of the alkalis do not give precipitates; but if acetic acid be added to a solution of albumin containing one of these salts, or if the salt be added to a solution containing acetic acid, a precipitate is formed. Many salts of the metals produce a precipitate when added to a solution of albumin, *e.g.* ferrous sulphate, ferric chloride, copper sulphate, silver nitrate, neutral and basic acetates of lead and mercuric chloride.

Potassium ferrocyanide throws down from an albumin solution containing acetic acid a precipitate free from potassium. Chlorine and bromine produce precipitates. Phenol coagulates albumin. Rennet does not produce a precipitate at ordinary temperatures.

*Proximate composition.*—Béchamp has isolated three different substances from the white of hen's egg. The first (*primovalbumin*) is thrown down by basic acetate of lead, it has a rotary power for polarised light of  $(\alpha)_D = -34^\circ$  and is coagulated by heat. The second and third substances are left in the filtrate after removing the first; they are both precipitated by an ammoniacal solution of the basic acetate, but can be separated by fractional precipitation. One of them (*secondovalbumin*) is coagulated and rendered insoluble in water by alcohol; it has a rotary power of  $-53^\circ$  and is coagulated by heat. The other (*leucozymase*) is precipitated by alcohol, but is not thereby rendered insoluble in water; it has a rotary power of  $-78^\circ$ , and is a ferment, as it possesses the power of liquefying starch paste. White of egg contains these substances in about the proportion of 5 : 4 : 1, and the rotary power  $-46^\circ$  calculated from these proportions agrees pretty closely with  $-40^\circ$ — $-43^\circ$ , the observed powers for white of egg.

#### Serum Albumin.

*Synonym.*—Blood albumin.

*Occurrence.*—It occurs in blood serum, muscle serum, lymph, chyle, milk, and abundantly in colostrum.

*Preparation.*—1. Blood serum is diluted with twentytimes its volume of water, and the globulin is thrown down by the cautious addition of acetic acid. After standing, it is filtered and the filtrate is neutralised with sodium carbonate, evaporated to a small bulk at  $40^\circ$ , and the greater part of the salts are separated by dialysis.—2. For technological purposes it is

prepared by collecting the blood straight from the animal in shallow zinc pans of about two gallons' capacity, in which it is left in a cool place until it has clotted; great care must be taken not to agitate it when fresh drawn, so the place must not be far from the animal. When it has completely clotted it is transferred to similar pans with perforated bottoms, and is cut into small fragments to allow the serum to drain away. The serum is collected and evaporated to dryness at a moderate temperature and the albumin is obtained in scales. All rough treatment must be avoided, as it causes the red corpuscles to break and spoils the colour of the product. Five oxen yield about  $4\frac{1}{2}$  gallons of serum and about  $4\frac{1}{2}$  lbs. of albumin. The blood of 20 sheep or 34 calves gives the same quantity of albumin. Less than half of the albumin only is obtained that analysis shows to be present in blood.

*Properties.*—Its properties are much the same as those of egg albumin, but its rotary power for polarised light is very different, being  $(\alpha)_D =$  from  $-56^\circ$  to  $-62^\circ$  (Haas), and, unlike egg albumin, it is not coagulated by shaking up with ether.

#### Crystallin.

*Synonyms and Occurrence.*—Crystallin (also called Globulin) is the name given to an albuminous substance obtained from the crystalline lens.

*Preparation.*—The crystalline lens is triturated and extracted with water, and the filtered extract is evaporated, some impurities are removed by alcohol, and a yellow mass is obtained.

*Properties.*—It is soluble in water, and is coagulated by heat, a granular mass being the result.

*Proximate composition.*—Béchamp has obtained two substances from the aqueous extract of the crystalline lens. One, *crystallalbumin*, is precipitated by the addition of alcohol; the precipitate, immediately after coming down, dissolves if water be added, but it is gradually changed into an insoluble state, and then addition of water does not dissolve it. It further differs from primovalbumin in giving a precipitate with basic lead acetate which is not decomposed by carbon dioxide. Its rotary power is  $(\alpha)_D = -80^\circ$ .

The other substance, *phacozymase*, is precipitated by alcohol, but is not thereby rendered insoluble in water. It is a ferment, as is proved by its liquefying starch paste. Its solution is coagulated by heat. Its rotary power is  $-41^\circ$ .

#### The Globulins.

##### Myosin.

*Occurrence.*—The fibres which enter into the composition of the voluntary muscles contain within an outer sheath a semifluid substance which is called the muscle plasma; after death, when *rigor mortis* sets in, this plasma yields a liquid (muscle serum) and a clot which causes the rigidity. This clot is myosin. Brine used for pickling meat contains a considerable quantity of myosin.

*Preparation.*—Fresh flesh is chopped fine and well washed with water until the washings are no longer acid and give no traces of the presence of any albuminoid; it is then triturated to a pulp with common salt, and enough



water is added to make with the salt a 10 p.c. solution. After standing for a time it is pressed through linen and filtered. The filtrate dropped slowly into water gives a precipitate of myosin, which can be purified by redissolving in sodium chloride solution and reprecipitating.

*Properties.*—When wet it forms a white mass, and when dry is yellow and horny. It is neutral in reaction. It is insoluble in water, alcohol, and ether. When suspended in water and heated to 70° it coagulates. It is readily soluble in dilute acids, and when thus dissolved the myosin changes into syntonin. It is soluble in dilute solutions of the alkalis and alkaline carbonates.

It dissolves readily in 1 to 10 p.c. solutions of sodium chloride, and is precipitated unchanged therefrom either by diluting with water or by saturating the solution with salt.

#### Serum Globulin.

*Synonyms.*—Globulin or Fibrino-plastic substance (Schmidt); Paraglobin (Brücke); Paraglobulin (Kühne).

*Preparation.*—Fresh blood serum is diluted with ten times its bulk of cold water and is subjected to a stream of carbon dioxide. The solution, after some time, deposits flocks, which are collected and dissolved in water with the help of a few drops of a very dilute solution of sodium hydroxide. The globulin is then reprecipitated by a stream of carbon dioxide.

*Properties.*—As precipitated, it is in microscopic, colourless, amorphous granules. It is insoluble in water, alcohol, and ether, but dissolves in water saturated with oxygen, and is thrown down again on passing carbon dioxide through the solution. It is readily soluble in dilute acids, but is changed by them into a derived albumin.

It is soluble in dilute alkalis and in alkaline carbonates. Dilute solutions of the alkalis change it into a derived albumin, unless they are extremely dilute, when the globulin can be thrown down by a current of carbon dioxide.

It is soluble in solutions of phosphates of the alkalis, sodium chloride, magnesium sulphate, and other salts. It is precipitated from its solutions in neutral salts by dilution with water, and the precipitation is helped by passing a current of carbon dioxide. It is also precipitated from solutions of neutral salts by increasing the amount of salt present to the point of saturation.

Globulin suspended in water, or dissolved in neutral salt solutions, is coagulated on heating to 70°.

It is not precipitated from its solution in acetic acid by potassium ferrocyanide.

#### Fibrinogen.

*Occurrence.*—Fibrinogen occurs in blood plasma—i.e. the liquid portion of blood before clotting has occurred; also in the liquids of hydrocele and of various serous cavities.

*Preparation.*—1. Blood plasma is diluted with 10 or 15 times its volume of ice-cold water and is subjected to a stream of carbon dioxide for a long time, to precipitate the globulin. This is separated and the liquid is further diluted, and on again passing carbon dioxide through it fibrinogen is precipitated. Fibrinogen can be separated from the other liquids

mentioned by similar treatment.—2. Horse's blood is mixed, immediately it escapes, with one third of its volume of a saturated magnesium sulphate solution. The corpuscles are then filtered off, and to the filtrate a saturated solution of sodium chloride is added which causes the precipitation of fibrinogen. The precipitate is removed, washed with more of the same sodium chloride solution, and is twice purified by dissolving it in a weaker sodium chloride solution containing 6 to 8 p.c., filtering and precipitating as before. As thus prepared it dissolves in water owing to the adhering salt.

*Properties.*—It is insoluble in water, but is soluble in water containing oxygen. It is soluble in dilute alkalis. Like globulin, it is soluble in solutions of sodium chloride; but when the salt reaches 12 to 16 p.c. the fibrinogen is precipitated, and but little globulin separates until the salt present amounts to 20 p.c.; this explains the second process of preparing it given above. Solutions of fibrinogen in sodium chloride coagulate at a considerably lower temperature than globulin solutions. When blood clots, the fibrinogen of the plasma is converted into Fibrin (*q. v.*).

#### Vitellin.

*Preparation.*—Yolk of egg, after treatment with water, alcohol and ether, leaves an albuminoid substance undissolved, to which the name vitellin has been given (Latin, *vitellus*, 'yolk of egg'). Various other methods for separating it from yolk of egg have been described, and possibly the products obtained are not identical.

*Properties.*—It appears to be insoluble in water, but soluble in dilute acids, alkalis, and in a 10 p.c. solution of common salt.

*Proximate composition of yolk of egg.*—Béchamp has obtained five substances from yolk of hen's egg. On treatment with water a granular substance is left, and in solution there is found a body (*lecithoinin*) which alcohol coagulates and renders insoluble; its rotary power when dissolved in acetic acid is ( $\alpha$ )<sub>D</sub> = -81°; also a second body (*lecithozymase*) which alcohol precipitates but does not render insoluble in water; it is a ferment and liquefies starch paste, its rotary power is about -48°.

The granular substance, after washing with ether, with ether containing a little alcohol and with water, is quite white and yields to a weak solution of sodium carbonate a body (*lecimicroönin*) which is precipitated on addition of acetic acid; its rotary power in acetic acid solution is -72° to -75°. The acetic acid filtrate contains a body (*lecimicrozymase*) which is thrown down on adding alcohol; it is soluble in water and is a ferment as it liquefies starch paste; its rotary power is about -81°.

The sodium carbonate leaves part of the granules undissolved, the substance left does not appear to be homogeneous, and it probably is the outer covering of the granules. It is this covering that prevents the extraction of the soluble *lecimicrozymase* by the water employed at first.

#### Derived Albumins.

##### Acid Albumin.

*Preparation.*—If egg albumin be treated with a little dilute hydrochloric acid, and the mixture be warmed gradually, no coagulation takes place even at 100°, and if when cold the solution be

neutralised, a precipitate is thrown down which is acid-albumin.

*Properties.*—It is soluble in dilute solutions of the alkalis and of the alkaline carbonates. It is insoluble in sodium chloride solution. It becomes coagulated when suspended in water and heated.

**Syntonin** (or *Musculin*) is a name given to the product of the action of dilute hydrochloric acid on myosin; the same name has been applied to the products obtained by the action of dilute acids on soluble or coagulated albuminous substances and on fibrin; syntonin has also been supposed to be formed as the first product of the action of the gastric juice on albuminous substances. Béchamp's experiments have led him to the conclusion that these products are different substances.

#### Alkali Albumin.

By the action of the caustic alkalis on egg albumin, substances are obtained which have received the names alkali albumin or albuminate. Most probably the products vary with the strength of the alkaline solutions employed and are numerous. If egg albumin is really a mixture of three different substances, some work has yet to be done before the products of the action of the alkalis are isolated and described.

The following are the most noticeable facts about the action of the alkalis on albumin.

1. If egg albumin is treated with dilute caustic alkali and the liquid warmed gradually, no coagulation takes place even at 100°; if the solution is allowed to cool and is neutralised by acid a precipitate is thrown down. This precipitate is called alkali albumin or albuminate.
2. If white of egg freed from membranes and then brought to its original strength is mixed with strong potash solution, it is converted into a gelatinous mass. This mass washed with water until the washings are no longer alkaline (access of air being prevented as far as possible) is soluble in boiling water. It has been called albuminate of potassium, being considered to be a salt of an 'albuminic acid.' From potassium albuminate, albuminates of copper, silver, and other metals have been obtained. When a solution of potassium albuminate is neutralised by an acid, a precipitate is thrown down which has been supposed to be the same as that obtained when dilute alkali is used as described above.

#### Casein.

*Occurrence.*—Casein occurs in the milk of mammals, and is the characteristic constituent of cheese (Latin, *caseus*) and from this its name is derived.

*Preparation.*—Fresh milk, diluted with its own bulk of water, is heated to 50°, and just enough acetic acid is added to make the liquid distinctly acid. The curd is separated on a cloth and well washed with water, a little acetic acid being added in the water first employed. The fat is next removed by treatment with a mixture of alcohol and ether, and then with ether alone. The mass is dissolved in very weak ammonia and the solution is filtered and precipitated by acetic acid. The precipitate is treated with ether, redissolved in ammonia and reprecipitated by acetic acid, washed with water, then with alcohol and ether, and finally dried

in *vacuo* over sulphuric acid (Béchamp).—2. For technological purposes, a preparation of casein known as lactarine is obtained by curdling skimmed milk with dilute acid or with rennet. The curd is collected, washed, and dried, and is sold in the form of a yellow granular powder.

*Properties.*—Casein appears to be a single compound, and not a mixture. Prepared as described above, it is a light, finely divided, white substance; other methods yield it as a yellowish, amorphous, hygroscopic mass, without taste or smell. That prepared by Béchamp contained only .2 p.c. of ash. Casein dried in *vacuo* retains water which requires a prolonged drying at 130°–140° to expel. Casein can be kept at 100° for some hours without being altered, but after heating to 130°–145° the product is no longer completely soluble in sodium carbonate solution.

Casein reddens litmus, and behaves like an acid to the alkalis and alkaline earths, and like a base towards the acids. It is insoluble in water, but dissolves readily in solutions of ammonia, the alkalis and the alkaline carbonates. Casein when still wet dissolves easily in lime water and in baryta water. Acids added to solutions of casein in the alkalis throw down precipitates which are compounds of casein with the acid; these compounds are decomposed by water, that with acetic acid most easily. Casein is readily soluble in dilute hydrochloric acid (containing .2 p.c. of the fuming acid), but addition of acid of medium strength to this solution throws down a precipitate containing hydrochloric acid. Casein is insoluble in hydrochloric acid containing 2 or 3 p.c. of the fuming acid. Casein dissolves in strong hydrochloric acid, giving a fine violet colour. Casein is soluble in aqueous acetic acid, forming an acetate; on evaporating the solution and drying, the acetic acid is not entirely expelled even at 140°.

Casein is insoluble in solution of sodium chloride. When still wet from its preparation, it dissolves in solutions of ordinary sodium phosphate and borax, which are alkaline. Casein in solution in potassium hydroxide is not coagulated by heat.

Casein has a rotary power varying from  $(\alpha)_D^{20} = -94^\circ$  to  $(\alpha)_D^{25} = -133^\circ$  according to the solvent employed.

*Curdling of Milk.*—When milk is exposed to the air, the milk sugar it contains is converted into lactic acid by the agency of a micro-organism (*Bacterium lactis*), and it becomes acid. This acidifying of the milk causes the precipitation of the casein, and the milk 'curdles.' In cheese-making another method of precipitating the casein is employed. Rennet, which is prepared by extracting the fourth stomach of the calf with a 5 p.c. solution of common salt, is added to the milk warmed to the temperature of about 25°, and causes the precipitation of the casein, which carries down the fat globules of the milk entangled in it. This curd, after subsequent treatment to remove the liquid, forms cheese. The precipitation of the casein has been shown to be due to the action of a ferment in the rennet, and not to the souring of the milk that accompanies the curdling.

*Fibrin.*

*Occurrence.*—Blood removed from the living animal soon turns to a jelly, which gradually contracts, squeezing out a liquid as it does so, so that eventually there is obtained a clot surrounded by a fluid (the *serum*). This clot is composed of fibrin with red blood-corpuscles entangled in it. Numerous theories have been advanced to explain this formation of fibrin; it is now supposed that the albuminoid fibrinogen contained in the plasma, *i.e.* the liquid part of living blood, yields fibrin under the influence of a ferment which is derived from the white cells of the blood, and is probably liberated by their breaking-up; some of the salts of the blood appear to be required also for the formation of fibrin.

*Preparation.*—Fresh blood is whipped with twigs, to which the fibrin adheres. It is next washed with water until colourless, after which it is treated with alcohol and ether to remove the fat. Blood plasma can be used instead of blood.

*Properties.*—Moist fibrin is a white, elastic, fibrous mass which becomes hard and friable when dried. It has no taste or smell. It is insoluble in water and in alcohol. When suspended in water and heated, or when kept for some time under alcohol, it undergoes a change and ceases to be soluble in saline solutions, and in dilute acids, but is still soluble in alkalis. Fibrin swells up and dissolves when digested in dilute solutions of the alkalis; these solutions are not coagulated by heat. Fibrin is coloured yellow by nitric acid, and on digesting, xanthoproteic acid is produced. In dilute hydrochloric acid, fibrin swells up and dissolves on gentle warming. In fuming hydrochloric acid, dry fibrin swells up and gradually dissolves to a dark-blue liquid. Strong acetic acid converts fibrin into a jelly which dissolves easily in warm water. In 6 to 10 p.c. solutions of the neutral salts, potassium nitrate, sodium chloride and sulphate, fibrin swells up, and the liquid can be filtered after long digestion; the solutions coagulate when heated.

Moist fibrin causes the evolution of oxygen from hydrogen dioxide; but loses the property after boiling.

The products of the action of dilute hydrochloric acid have been studied by Béchamp. A part of the fibrin is left undissolved (the *epidermose* of Bouchardat), consisting of microscopic granules, which, when washed free from acid, possess the power of liquefying starch paste and of liberating oxygen from hydrogen dioxide. These granules he regards as being organised, and names them *fibrin microzymes*. They still liberate oxygen after being dried *in vacuo*, but after boiling in water this property is lost.

The solution freed from the microzymes gave a rotary power of  $(\alpha)_D = -72^\circ$ , calculated on the matter obtained by evaporating and drying at  $110^\circ$ – $120^\circ$ . Addition of ammonia to it throws down a substance which he names *fibrinin*. It is insoluble in water but dissolves readily in aqueous acetic acid, and gives a rotary power of  $(\alpha)_D = -67^\circ$ . In fuming hydrochloric acid it dissolves, and on warming gives a fine violet colour.

The filtrate from the fibrinin, when mixed with a large quantity of alcohol and a little sodium acetate solution, gives a precipitate which is nearly all soluble in water. This soluble substance he names *fibrimin*. It possesses a rotary power of from  $(\alpha)_D = -79^\circ$  to  $(\alpha)_D = -87^\circ$ . When dry it dissolves in fuming hydrochloric acid, and gives on warming a mauve-red colour, changing to a brownish-red. Its solution is not coagulated by heat, or precipitated by neutral or basic lead acetate; it is precipitated, however, by metaphosphoric acid. Nitric acid turns its solution yellow; Millon's reagent gives a slight precipitate and a red colour on warming. It has the power of liquefying starch paste, but only in a feeble degree.

According to Béchamp, there appear to be other products besides these.

*Gluten.*

*Preparations.*—1. The mixture of substances left when wheat flour is made into dough and kneaded with water until no more starch is washed away, is known as gluten, or wheat-gluten.—2. For use in dyeing, the gluten obtained as a by-product in the manufacture of starch from wheat has been employed. The process used in the manufacture consists in washing the starch away from the gluten, and then allowing the starch to settle from suspension in water; there are various ways of effecting this: in one the grain is steeped in water, crushed between rollers, and then kneaded on a sieve with water, when the starch is washed through and the gluten is left on the sieve.

*Properties.*—In the moist state it is a light-yellow, tough, elastic, and adhesive mass; when dried it is brown, translucent at the edges, and brittle. Moist gluten, when heated, coagulates and becomes for the most part insoluble in alcohol, acids, and solution of caustic potash; the same change is effected when it is dried by heat. When moist gluten is kept, it soon gives off carbon dioxide and liquefies to a varnish-like mass.

Boiling water dissolves out some of the constituents of moist gluten. Gluten is only partly dissolved by boiling alcohol. It is insoluble in ether.

Dilute hydrochloric acid dissolves gluten, giving a solution which becomes turbid on boiling, and with which acids give precipitates soluble in excess of the precipitant. Dilute acetic acid dissolves gluten, whether fresh or dried, without heating. These acids, however, leave the impurities of the gluten, *viz.* starch, fat, &c., undissolved. Gluten swells up and falls to pieces in aqueous ammonia, but does not dissolve. Fresh gluten dissolves in solutions of caustic potash and soda; these solutions are precipitated by the addition of acids; in the case of phosphoric and acetic acids the precipitate separates when the alkali is just neutralised, and dissolves on adding more of the acid.

*Proximate composition.*—Besides water, fresh gluten contains a certain amount of starch grains, fat, and other debris; the rest of it is composed of several substances which have been differently named by different authors. Béchamp, by the use of alcohol and of 1 p.c. hydrochloric acid as solvents, isolated four substances, *viz.* (1) gluten, which is soluble in alcohol; (2) plant casein, which is soluble in water; (3) gluten-



fibrin, which is soluble in .1 p.c. hydrochloric acid; and, (4) a gluten-fibrin which, when isolated, is insoluble in acid of that strength, although in the original gluten the presence of gluten enables it to dissolve in dilute hydrochloric acid.

#### Technological Uses.

*Dyeing.* Egg albumin and blood albumin are largely used as mordants in dyeing and printing calico and to some extent in printing wool.

Albumin is used to fix two classes of colours, the action being somewhat different in the two cases. Those colours which are employed in an insoluble condition, *e.g.* ultramarine, are mixed in the cold with a solution of albumin and printed on the calico, which is afterwards steamed. The heat coagulates the albumin, and this incloses the colour and fixes it permanently on the fibre. The other class of colours which are employed in solution, *e.g.* many of the aniline dyes, have the power of combining directly with the animal fibres, wool and silk, to form compounds which can withstand washing; they do not, however, form such compounds with vegetable cellulose fibres, and the difficulty is met by 'animalising' these fibres by coagulating albumin on to them; after this treatment the dye combines with the albumin as it does with wool and silk, and becomes fixed to the fabric. The solution of albumin is printed on to the calico, or if the whole cloth is to be dyed the calico is impregnated with albumin solution and dried. The albumin is then coagulated by steaming, and the fabric is dyed in a solution of the colour which only attaches itself permanently where the albumin has been applied. Another method employed is to print the albumin and the soluble colour together on the calico and then to steam. In using albumin for various colours, thickening agents are in some cases mixed with it.

Blood albumin is cheaper than egg albumin and can be obtained in nearly as colourless a condition. A given quantity of it has a greater thickening power than the same quantity of egg albumin, but for light colours it does not answer so well owing to its tint, and further it seems to acquire more colour from the dirty soap liquor used in a subsequent operation than egg albumin does.

A preparation of casein, known as lactarine, is used as a substitute for albumin; it was introduced by Pattison in 1848 for fixing pigment colours, and later it was also employed for soluble colours. Lactarine is insoluble in water, but with ammonia solution it yields a smooth white paste, which is employed in the same way as albumin; the steaming drives off the ammonia, and leaves insoluble casein on the fibre. Other solvents employed or proposed are caustic soda, borax and acetic acid. As left by the driving off of the ammonia, the casein is soluble in alkaline solutions, but if the ammonia paste is mixed with fresh milk of lime and then applied to the cloth, on heating a lime cement is formed on the fibre which can withstand washing with alkaline liquids. Lactarine is inferior to albumin as a mordant, and is apt to give trouble in working, as the paste seldom keeps good for twenty-four hours.

Skim-milk cheese can be used instead of lactarine to furnish the casein; it is macerated with warm water to remove salts and fatty matters, and then the paste is prepared with ammonia or caustic soda as in the case of lactarine.

Another substitute for albumen is gluten, but it has not been largely used. There are various methods of getting it into solution; one method is to leave the moist gluten until it becomes sour and fluid; it is then treated with sodium carbonate to render it insoluble again, and after having been washed it is dissolved in caustic soda solution, or else the treatment with sodium carbonate is omitted, and the sour and fluid gluten is mixed at once with caustic soda solution. Another method is to leave the moist gluten until it is plastic, dry it, and then dissolve it in saccharate of lime.

*Photography.*—Albumin is largely used in photography for various operations. One important use is in preparing the sensitive paper on which the positives are printed from the glass negative plate. The paper is first floated on a solution containing albumin and a soluble chloride, and is then dried. It is next sensitised by floating it on a solution of silver nitrate; the result is a film containing silver chloride and nitrate, and a compound of silver and albumin, which is darkened by light. The silver bath must be of sufficient strength, otherwise the albumin is not rendered insoluble.

Albumin is also used for the negative plate, in dry plate processes, a film of it is sometimes put on the plate to form a stratum unting collodion to the glass so that it may adhere during the subsequent treatment; it is also used in some of the preservative liquids applied after sensitising. In one process the film on the glass before sensitising is formed of albumin containing potassium iodide.

In photography, egg albumin is preferred to blood albumin; either white of egg or the dried albumin of commerce is employed.

*Sugar refining.*—In refining sugar, the syrup obtained by dissolving the raw sugar contains suspended impurities; these were formerly removed by adding blood serum or fresh blood, and heating to coagulate the albumin which entangled the suspended matters. This method has been replaced, and the suspended matters are removed by filtering through cotton bags.

H. H. R.

**ALCOHOL** (Ethylic or Vinous), the active principle of intoxicating liquors, is, in the dehydrated condition, a colourless liquid having a specific gravity of .791 at  $20^{\circ}$  (Lowitz, Crell's Ann. 1, 1796, 1-195), .7938 at  $56^{\circ}$  (Fowncs, Tr. 1847, 249), .793811 at  $15.6^{\circ}$  (Drinkwater, P. M. Feby. 1848), .79350 at  $15.6^{\circ}$  (Squibb, Ephemeris, 1884-5, and Ph. [3] 16, 147-148). It boils at  $78.4^{\circ}$  under a pressure of 760 mm. (Kopp, A. 92, 9), and solidifies at  $-130.5^{\circ}$  (B. Wroblewski and H. Olsewski, C.R. 96, 1140-1142 and 1225-1226). It is inflammable, the combustion evolving great heat but little light, and producing carbonic anhydride and water. It acts as a caustic irritant in contact with the tissues of the body,

owing probably to the energy with which it draws moisture from the surface. It possesses a specific heat of 0.6120, calculated at temperatures between  $16^{\circ}$  and  $40.5^{\circ}$  (Schüller, P. Erg. 5, 116-192). Its index of refraction for  $H\beta = 1.3667$  (Brühl), and its critical temperature  $234.6^{\circ}$  at 48.9 m. At this point 1 gr. occupies 3.5 c.c. (Ramsay and Young, Pr. 38, 329).

Alcohol forms ethoxides with sodium and potassium, and unstable compounds with certain crystalline salts, e.g. zinc chloride, the latter called alcoholates. Subjected to the action of a limited supply of oxygen it is converted into aldehyde ( $C_2H_4O$ ), which, by further oxidation, becomes acetic acid ( $C_2H_4O_2$ ). Distilled with chloride of lime, it forms chloroform ( $CHCl_3$ ). With sulphuric acid at a temperature not exceeding  $145^{\circ}$  it yields ether ( $C_2H_5O$ ). With twice its bulk of sulphuric acid it gives ethylene ( $C_2H_4$ ). With excess of dry chlorine gas it produces chloral ( $C_2H_3ClO$ ).

*Preparation.*—Synthetically from its elements thus:—By passing an electric arc between carbon poles in an atmosphere of hydrogen acetylene ( $C_2H_2$ ) is produced, which, in the presence of nascent hydrogen, becomes ethylene ( $C_2H_4$ ). Ethylene by protracted shaking with sulphuric acid is converted into sulphovinic acid, which, being distilled in presence of water, produces alcohol.

Alcohol is, for practical purposes, prepared by dehydrating the products of the distillation of fermented liquids. Up to 1795 the strongest spirit known contained not less than 5 per cent. of water. Lowitz appears to have been the first to prepare it in an approximately anhydrous condition. His process consisted in first increasing the strength of rectified spirit by adding to it dry potassic tartrate, and after decanting from this, distilling very slowly in presence of great excess of perfectly dry potassic carbonate. Richter used, instead of potassic carbonate, hot calcium chloride (Crell's Ann. 2, 211). Drinkwater first digested with perfectly dry potassium carbonate for twenty-four hours; decanted the strong spirit thus produced, digested with as much fresh-burnt quicklime as was sufficient to absorb the whole of the alcohol, and afterwards distilled in a water-bath at a temperature of  $82.2^{\circ}$ . The product of this distillation, which was found to have a specific gravity of .7946 at  $15.6^{\circ}$ , was returned to the retort, and a fresh quantity of dry pulverised quicklime added to it, after which it was allowed to digest for a week at a temperature of  $15.6^{\circ}$ . It was then again slowly distilled and the specific gravity of the product found to be .7944 at  $15.6^{\circ}$ . This was digested at a temperature of  $54.4^{\circ}$  with hot quicklime, and distilled out of contact with the air at a temperature of  $81.1^{\circ}$  to  $82.2^{\circ}$ , and the specific gravity of the product, which was taken as absolute alcohol, found to be .793311 at  $\frac{15.6^{\circ}}{15.6^{\circ}}$ .

Dr. Squibb followed the process of Drinkwater, distilling in a partial vacuum of 330 to 630 mm., and making use of the Sprengel pump to produce perfectly dry air in the bottles. The alcohol he thus prepared had a specific gravity of .79350. The difference between this specific gravity and that found by Drinkwater only represents one-tenth per cent. of alcohol. Men-

déléef's observations (Z. 1865, 260, and P. 138, 103, 230) practically confirm those of Drinkwater and Fownes.<sup>1</sup>

*Tests.*—We are dependent upon specific gravity for the exact quantitative estimation of alcohol, and perhaps no method could be devised so easy of application (v. ALCOHOLOMETRY). It is, however, open to the objection that it assumes water to be the only volatile substance with which the spirit is mixed, aldehyde, fusel oil, and ether when existing as impurities being reckoned as alcohol. On the other hand, no chemical test, capable of practical application, has yet been devised for the exact quantitative estimation. Berthelot's process (C. R. 80, 1039) of measuring the ethylene produced by sulphuric acid and absorbed by bromine from a given quantity of spirit is a valuable qualitative test, and within limits most useful when applied quantitatively in presence of methylic alcohol. The production of iodoform (Hager, C. R. 82, 768) may be employed with advantage as a preliminary test for small quantities of alcohol, but as other bodies produce iodoform under the same circumstances, it cannot be regarded as conclusive. For the detection of alcohol in ether Allen (C. J. 2, 1877, 930) suggests that a little fuchsin be shaken up with water and ether, and 10 c.c. of the solution thus formed agitated with the same quantity of the ether submitted for examination; the intensity of the colour produced would be a measure of the quantity of alcohol present. For the detection of fusel oil in alcohol A. Jorissen (B. C. 1881, 791) recommends that 10 c.c. of the spirit should be mixed with 10 drops of colourless aniline and 2 or 3 drops of sulphuric acid. A deep-red colour would thus be formed if fusel oil be present, due to the action of furaldehyde, an invariable impurity in fusel oil.

Alcohol is sometimes used as an adulterant in essential oils. A very ready test is to place a little of the oil in a perfectly dry test-tube, taking care in pouring it in that none adheres to the side. Rub a little fuchsin on the upper inside surface of the test tube and apply heat, the presence of alcohol will be indicated by red stains in the fuchsin. No satisfactory test has yet been suggested for the estimation of aldehyde in alcohol, but the peculiar suffocating odour which accompanies it, and the brown colour produced by alkalis in the spirit, are characteristic of its presence.

*Manufacture.*—The first process in the manufacture of spirit is one of brewing, and in general principles it does not differ from that employed in making beer. The brewer, as well as the distiller, endeavours to treat his materials in such a way as to extract from them the greatest amount of fermentable matters. The brewer of beer, however, does not desire to convert all the matter he extracts into spirit, and he brews at such gravities as his customers require. The distiller desires to convert as much as possible of the matter he has extracted from his materials

<sup>1</sup> Absolutely anhydrous alcohol produces no blue colouration with dehydrated (white) copper sulphate. It should give no cloudiness when mixed with benzene. Absolutely anhydrous alcohol added to a mixture of anthraquinone (.001 gr.) with a little sodium amalgam gives a green colouration; if a trace of water be present the colour becomes red (Claus, B. 10, 927).



into spirit; he therefore produces a wort containing more maltose and less dextrinous matter than the brewer of beer. He has also an advantage over the brewer in being able to choose the gravities which he knows by experience will produce the best results. It has been found that for distillers' purposes it is advisable to keep the specific gravity of the wort when set for fermentation below 1040°. The principle of low temperatures when the diastase is acting in the mash tun appears to be fully recognised, 60° to 63° being generally adopted, and it is understood that the higher the temperature at which the worts are set for fermentation, the greater is the amount of fusel oil in the spirit. The distiller has, therefore, to choose the lowest temperature at which a healthy fermentation can be started, and this is found to range between 23° and 25°. He cannot be too careful as to the purity of his yeast, for not only has he to run the risk of acetic and other ferments being introduced into his wort, involving loss of alcohol, but to provide against the presence of aldehyde which is so objectionable in his spirit. Kekulé attributes the presence of aldehyde to the action of nitrates derived from the materials. It is found in practice that it is always more prone to appear in hot weather, when the difficulty of keeping the yeast from decomposition is greatest, and as yeast always contains some spirit in a dilute form it is not improbable that the aldehyde is frequently a product of the oxidation of this spirit.

The materials used in the manufacture of alcohol in the United Kingdom are chiefly malt, maize, rice, barley, rye, oats, sugar, and molasses, but occasionally dates and locust beans have been employed. In Scotland the smaller distillers use malt only, and the spirit they produce under the name of Highland, Campbeltown, or Islay Whiskey, Glenlivet, Lochnagar, &c., has imparted to it a flavour derived partly from the peat used in drying the malt. The process of manufacture consists in distilling the fermented wort—then called wash—in a common still, collecting the distillate, which is weak spirit contaminated with fusel oil, and is called 'Low Wines,' and redistilling. The spirit which passes over in the middle of the redistillation is that which is used for consumption. It contains from 60·8 to 76·7 per cent. of alcohol by weight (20 overproof to 45 overproof), but is generally diluted by the addition of water to 55·4 per cent. of alcohol by weight (11 overproof) before being sent into consumption or placed in bond. Irish whiskey differs from Scotch chiefly in the absence of peat flavour. The materials used in its manufacture are, with one or two exceptions, a mixture of malt and grain, the proportion of malt being, however, greater than in English distilleries. It is generally bonded at 25 overproof (64 per cent. of alcohol by weight).

We have hitherto dealt with the spirit manufactured in 'Common' or 'Pot' stills, or in other words by boiling the wash, condensing the steam thus produced, reboiling the product and recondensing. But by far the greater quantity of the alcohol of commerce is produced by the Coffey still, in which the alcoholic vapour having been produced is deprived of water as the process continues until a spirit is formed of much greater purity than that manufactured

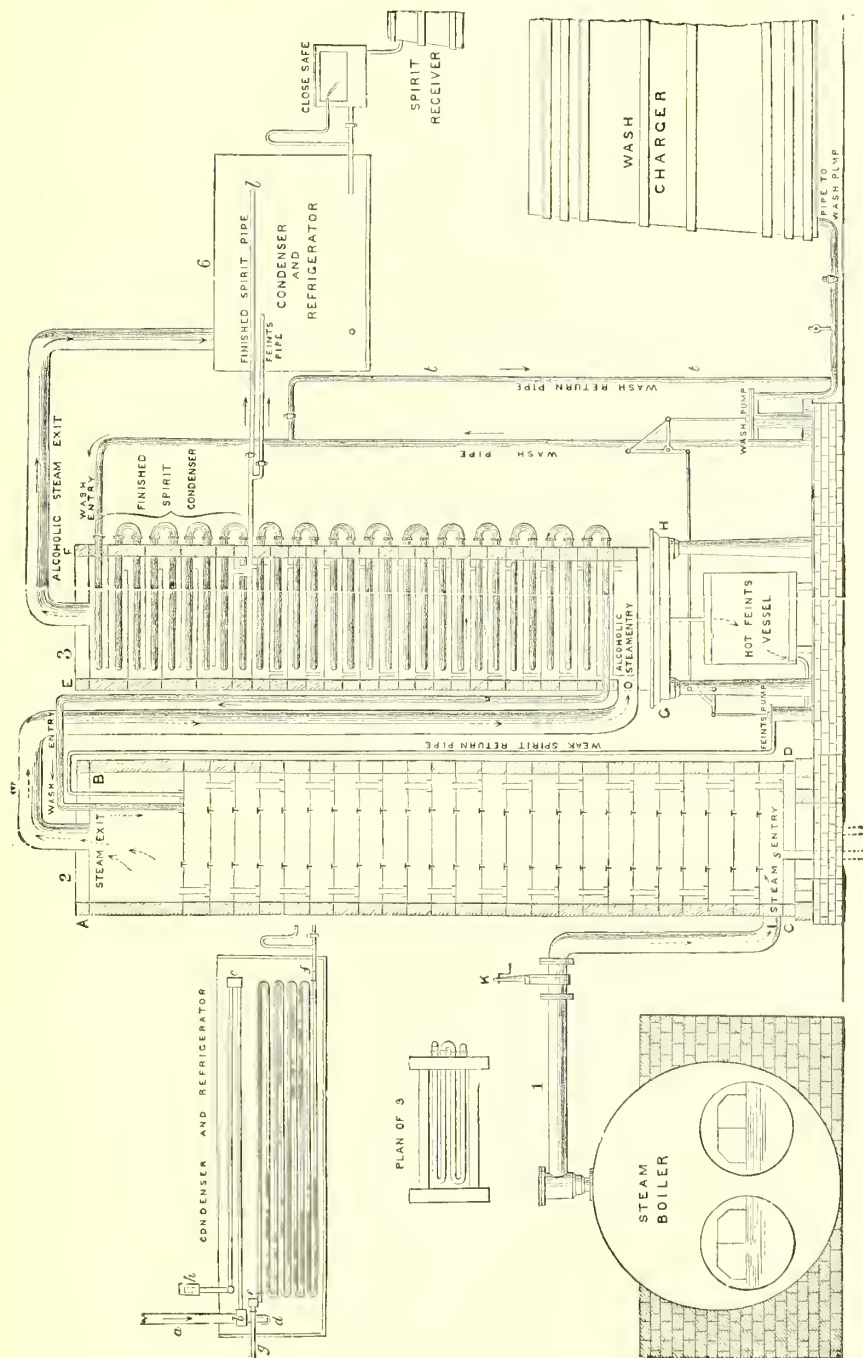
by the old method. The annexed sketch represents a Coffey's distilling apparatus, the left hand column being called the *analyser*, the right hand one the *rectifier*. The first operation is to fill both columns with steam. This is accomplished by introducing it under pressure from the boiler at c, whence it ascends within the analyser, passing by the pipe m into the bottom of the rectifier. When a proper temperature has been attained, the wash is pumped from the wash charger by a pipe which enters the top of the rectifier. This pipe is only shown sectionally in the sketch after entering the column, but it is continuous, and the wash passes slowly through it, becoming warmer, owing to the pipe being in contact with the steam. When it has reached the bottom of the rectifier it is not far from the boiling-point. It will be seen that the pipe then ascends, and finally delivers the wash into the top of the analyser. The lines across the analyser represent plates of perforated copper, and in connection with each is a tube which projects about an inch and a half above the plate, and dips into a shallow vessel placed on that next beneath. The wash on entering falls on the first plate, but on reaching a depth of an inch and a half passes through the tube to the second one. In the meantime the steam produces ebullition in the contents of the plates, and carries away with it the alcoholic vapour through the steam exit pipe, so that by the time the wash has reached the bottom of the column it has been deprived of its alcohol. The alcoholic vapour passes by the pipe m into the bottom of the rectifier, which like the analyser contains plates and metal tubes, and where a process of gradual cooling takes place by the action of the pipe carrying the cold wash. Fusel oil vapour, condensing at a higher temperature than alcohol, is the first to assume the liquid form, and contaminated with spirit passes into the hot 'Feints' receiver. The vapour containing alcohol continues to ascend, meeting with portions that have condensed, and are undergoing the process of rectification. It will be seen that the upper part of the apparatus is marked off in the sketch as finished spirit condenser. It is so called because all that condenses within its area, instead of returning towards the bottom of the apparatus to be rectified, passes by the finished spirit pipe or Feints pipe into the receivers. At the top of the apparatus is a pipe marked 'alcoholic steam exit' which carries away most of the aldehyde as well as spirit vapour which under special circumstances may not have been condensed before reaching that point.

The English distillers confine themselves exclusively to this apparatus, brewing for the most part from a mixture of grain and malt. The spirit produced does not to any large extent go into consumption as whiskey, the want of flavour being an objection in regard to the better qualities. Large quantities are transferred to the rectifiers who redistil them with various flavouring ingredients, producing gin, British brandy, British rum, and the various cordials. A portion after being redistilled from potash or potassic carbonate, or filtered through charcoal, is used in the arts and in medicine under the names of rectified spirit and spirits of wine.



The British Pharmacopœia (1885) requires rectified spirit to be of a specific gravity of  $\cdot 838$ , equal to 84 per cent. of alcohol by weight. The Pharmacopœia of the United States fixes it at  $\cdot 820$ , equal to 91 per cent., which is about the strength it comes from Coffey's apparatus. It

is from this spirit that anhydrous or absolute alcohol is generally prepared. It varies considerably in flavour and according to the United States Dispensatory, 1883, the purest is produced under Atwood's patent in which permanganic acid is used to destroy the disagreeable organic



substances. It has been suggested that the purity of strong spirit might be considerably increased by redistilling *in vacuo*. Reference has already been made to the occurrence in variable quantity of secondary products on fermentation. Pasteur (A. Ch. 58, 330) has shown that on the fermentation of sugar 3.16 per cent. of glycerin and 0.67 per cent. of succinic acid is produced. These bodies are, however, very slightly volatile, and therefore can only pass into the spirit in very small proportion.

We have hitherto confined our remarks to spirit manufactured in the United Kingdom. Of those possessing importance abroad, the principal is brandy, the production of which from grape wine is an industry confined almost entirely to France. The best brandy is derived from white wine, but a considerable quantity of spirit is imported from the Continent, under the name of brandy, which has either been mixed with other spirits or prepared from substances bearing no relation to wine. The distillation of genuine brandy takes place in stills which are practically on the pattern of common or pot stills; the improvements being chiefly confined to the adoption of means for carrying on the distillations continuously. Illustrations of the various stills now in use will be found in Duplais' treatise on the manufacture and distillation of alcohol. Brandy is generally imported into this country at a strength of 1 or 2 overproof (50 per cent. of alcohol by weight) (*v. BRANDY*).

Rum is the spirit produced by fermenting diluted molasses and distilling the product in an ordinary still. Its character is due to the formation of ethyl butyrate, which, when added to other spirits, produces a flavour difficult to distinguish from genuine rum. The strength at which rum is generally imported into this country is about twenty overproof (60.8 per cent. of alcohol by weight) (*v. RUM*).

The molasses from the beet sugar manufactories in France is now utilised in making spirit, being simply neutralised, generally mixed with a little rye flour and malt, fermented and distilled. The best qualities of spirits thus produced are according to Duplais devoid of taste or any peculiar aroma, and are employed in the manufacture of liqueurs, for improving common brandies and for refining rectified spirit.

Geneva or Hollands is a well-known form of gin manufactured in Holland where the grain spirit is for the most part made from a mixture of malt and rye. It does not possess any characteristic to distinguish it from the same article manufactured by rectifiers in this country, and its consumption appears to be declining (*v. GIN*). Absinth now largely consumed in France is also a form of gin in which the spirit is flavoured with the bitter principle of wormwood, together with extracts of some or all of the following plants: fennel, hyssop, anise, coriander, angelica seed, dried veronica, chamomile and mint (*v. ABSINTH*). A large quantity of spirit manufactured in Germany from potatoes is imported into this country, coming into competition with the lowest qualities of spirits of wine of the British distilleries.

Reference has already been made to the bonding of whiskey—that is, placing it in warehouses

under the control of the revenue authorities where it remains maturing for periods varying from a few months to several years. The exact change which takes place during the maturing process has not yet been satisfactorily explained, although the labours of Pelletan, Dumas and Stas, Gaultier, Chancel, Wurtz, Cahours, Balard, Liebig and Pelouze, Pasteur, Fittig, and Krämer and Pinner have added largely to our knowledge of the subject. According to the researches of these authorities fusel oil is a complex substance and a necessary accompaniment to fermentation. In grain fermentations amyl alcohol is the predominant constituent of this oil, but propyl and butyl alcohol are also present. In wine fermentations it consists principally of amyl and caproyl alcohols. It is probable that these alcohols are converted, in the process of maturing the spirit, from a disagreeable smelling and highly intoxicating body into compound ethers which are both fragrant and harmless.

In the process of mellowing there is generally a loss of alcohol, varying with the length of time and the condition of the atmosphere of the warehouse. The revenue authorities fully recognise this, and make the necessary allowances in charging the duty. It will therefore be apparent that alcoholic strength based on specific gravity is not always a measure of the money value of spirits as beverages. The Food and Drugs Amendment Act (42 & 43 Vict. c. 30) has fixed a limit below which spirits shall be assumed to be diluted. This limit is twenty-five under proof (35.8 p.c. of alcohol by weight) for whiskey, brandy, and rum; and thirty-five under proof (30.8 p.c. alcohol by weight) for gin.

*Uses.*—In addition to its use as a beverage, spirit is employed as a solvent for many of the drugs required in medicine, and diluted to the standard of British proof—that is, to the specific gravity of .91984 at 15.6°, representing 49.24 p.c. by weight of Drinkwater and Fownes alcohol—it forms part of a large proportion of the tinctures of the *Materia Medica*. It is also used largely as a solvent for essential oils, in preparing perfumes and essences, and ether is manufactured from it. The alcohol used in all the above preparations pays a duty of 10s. per proof gallon, equal to very nearly 18s. 4d. per gallon of the alcohol of Gay-Lussac, the standard of France.

*Adulteration.*—Although it has been stated that spirits, especially gin, were formerly adulterated with capsicum and even sulphuric acid, in order to increase their fiery character, it is satisfactory to find that in the working of the Food and Drugs Act no evidence has been afforded of such practices during late years. The report of the Local Government Board, 1885, after referring to the fact that one-fourth the samples submitted for analysis were diluted below the standard, adds, 'It is satisfactory, however, to find that water is the only adulterant employed.'

*Methylated spirit.* In 1853 a strong representation was made to the Government to allow the use of alcohol duty-free in the arts and manufacturing processes in which it was required, and after careful inquiry the Board of Inland Revenue in 1855 decided to sanction

under certain restrictions a mixture of nine parts of spirits of wine and one part of methyl alcohol (wood naphtha) free of duty under the name of methylated spirits. The reasons for selecting wood naphtha were that while it would be least likely to interfere in any of the processes for which alcohol was required—especially as a solvent—it would be very difficult to separate from the alcohol when once mixed. It was provided that it should not be used in any leverage, or medicine which could be taken internally. The principal restriction on the use of methylated spirit is that it shall only be kept by authorised persons and in authorised premises.

*Uses.*—Methylated spirit is used as a solvent for gum resins, including varnishes, for burning in lamps, in the manufacture of transparent soap, collodion, aniline colours, white lead and acetate of lead. It is also used as an antiseptic in preserving anatomical specimens. The consumption of this spirit has increased from 145,000 bulk gallons in 1857 to 1,900,000 in 1887.

The following are the quantities of British and Foreign spirits consumed in Great Britain and Ireland, and British spirits exported calculated in gallons at proof.

Year ending 31st March	Spirits charged with duty. Gallons		Total charged with duty. Gallons	Spirits methylated. Gallons	British spirits exported. Gallons	Spirits consumed as ships stores. Gallons
	British	Foreign				
1875	29,821,574	11,779,720	41,601,294	1,180,000	2,101,875	655,595
1885	29,224,474	8,349,360	37,573,834	2,334,835	3,832,545	351,250
1886	27,551,982	8,098,400	35,650,382	2,477,798	4,095,785	359,178
1887	26,935,873	8,168,060	35,103,933	2,673,375	3,960,819	326,150

Quantities of British and Foreign spirits consumed in Great Britain and Ireland, and British spirits exported calculated in *gallons of alcohol* of Gay-Lussac.

Year ending 31st March	Spirits charged with duty. Gallons		Total charged with duty. Gallons	Spirits methylated. Gallons	British spirits exported. Gallons	Spirits consumed as ships stores. Gallons
	British	Foreign				
1875	17,207,040	6,796,890	24,003,930	680,891	1,039,680	378,270
1885	16,862,520	4,817,580	21,680,100	1,347,190	2,211,370	204,400
1886	15,897,490	4,672,770	20,570,260	1,429,680	2,363,260	207,240
1887	15,541,990	4,712,970	20,254,960	1,542,530	2,285,380	188,180

The quantity of Foreign spirits exported in 1875 was 3,045,042 proof gallons. In 1885 it was 2,157,201 proof gallons. G. N. S.

**ALCOHOLOMETRY** is the term applied to any process for estimating the amount of alcohol in a spirituous liquid. When the liquid is a mixture of alcohol and water, the quantity of alcohol can be indicated by its specific gravity; but when it holds in solution other bodies, they must be separated by distillation and replaced by water before the specific gravity can be ascertained.

When two liquids, on being mixed, neither contract nor expand, the specific gravity of the mixture can be readily ascertained by the well-known formula—

$$\frac{r_1 d_1 + r_2 d_2}{r_1 + r_2} = x,$$

$r_1$  and  $r_2$  representing respectively the volumes of the components, and  $d_1$  and  $d_2$  their densities. In the case of mixtures of alcohol and water,

*Tests.*—For the detection of methylated spirit in ordinary alcohol, Riche and Bardy (C.N. 31, 239) recommend the distillation of 10 c.c. of the alcohol with 15 gr. of iodine and 2 gr. of red phosphorus, and the conversion of the methyl or ethyl iodide, which distils over, into methyl or ethyl aniline. Methyl aniline on being oxidised produces the well-known violet, and the intensity of the colour dyed on a piece of white wool 2 feet in length with a very dilute solution of the aniline violet is the measure of the proportion of methyl alcohol present. The test when carefully performed produces satisfactory results, but its application, as indeed that of all tests, must be preceded by the separation of the alcohol from all organic matter. Another test called Miller's (Ph., April 1865) is to oxidise the alcohols with potassium bichromate, and estimate the formic acid thus produced.

Gunning's test (C.N. 17, 186 and 196), a modification of that of Nessler, is a useful preliminary test where strong spirit is being dealt with.

however, contraction takes place varying in amount according to the proportion of alcohol to water in the mixture.

It has therefore been found necessary to ascertain by actual experiment the densities of mixtures of alcohol and water in all proportions and at various temperatures. The results of these experiments are embodied in tables, generally associated with the names of those who carried out the investigations. In 1794 Sir Charles Blagden, in conjunction with Mr. Gilpin, concluded a very extensive and careful series of experiments, undertaken at the request of the British Government (Tr. 1794), which have been generally recognised as accurate, and accepted by some of the Continental governments as the basis of their systems. At that time anhydrous alcohol had not been prepared,



and the experiments were made with spirit having a specific gravity of  $\cdot 825$  at  $\frac{15.6^\circ}{15.6^\circ}$ . Tralles, who in 1811 was engaged in a like investigation for the Prussian Government (G. A. 1811), confirmed the researches of Blagden and Gilpin. He also found by experiment that spirit of the specific gravity of  $\cdot 7986$ —the strongest he had been able to prepare—must contain 9.63 p.c. by weight of water when reduced to the specific gravity of  $\cdot 825$ . In the meantime, Lowitz and Richter had prepared alcohol of the specific gravity of  $\cdot 7939$  at  $\frac{15.6^\circ}{4^\circ}$  or  $\cdot 7946$  at  $\frac{15.6^\circ}{15.6^\circ}$ . Tralles therefore accepted this specific gravity as that of pure alcohol, and calculated the composition of the spirit of Gilpin and Blagden as—

Alcohol by weight . . . 89.2 p.c.  
Water     "     "     "     10.8 "

100.0

and alcohol by volume 92.6 p.c. He also carefully tested and substantially confirmed the results Blagden and Gilpin obtained by mixing strong spirit and water in all proportions, and upon these data constructed the tables now in general use in Germany. Gay-Lussac undertook similar researches for France. Beginning with alcohol of the specific gravity of  $\cdot 7947$  at  $\frac{15^\circ}{15.6^\circ}$ , or

$\cdot 7944$  at  $\frac{15.6^\circ}{15.6^\circ}$ , his results do not in every case exactly accord with those of Tralles, but they are sufficiently alike to be used for all commercial purposes. The whole subject has been investigated by McCulloch for the Government of the United States (Senate document No. 50, 1848), who practically confirms the previous results, and on whose recommendation a system has been adopted by the revenue authorities in which 50 p.c. by measure of Tralles' alcohol at  $\frac{15.6^\circ}{4^\circ}$  being called 100 degrees of proof spirit, every degree of American proof is equal to  $\cdot 5$  p.c. of Tralles' alcohol.

The most definite form of expressing the proportions of alcohol in spirit is by weight, because the proportion by volume varies with the temperature, whereas that by weight is constant. For scientific purposes, therefore, the strength of spirit is always expressed in percentage by weight, and this is found by taking the specific gravity by means of a specific gravity bottle at the temperature of  $15.6^\circ$ .

The annexed table compiled by Fownes (Tr. 1847) gives the percentage by weight of alcohol of the specific gravity of  $\cdot 7938$  at  $\frac{15.6^\circ}{15.6^\circ}$  corresponding to various gravities, and can be easily interpolated for any intermediate gravity.

Drinkwater made mixtures of alcohol of specific gravity  $\cdot 7938$  at  $\frac{15.6^\circ}{15.6^\circ}$  with from 99 to 90 p.c. of water. His results differ slightly from those given in the table of Fownes, the specific gravities for 7, 8, 9 and 10 p.c. of alcohol being respectively  $\cdot 9881$ ,  $\cdot 9867$ ,  $\cdot 9853$  and  $\cdot 9839$ , representing differences of from  $\cdot 15$  to  $\cdot 18$  p.c. of alcohol. Squibb also made mixtures of alcohol of  $\cdot 7935$  with from 1 to 60 p.c. of water, the greatest discrepancy between his results and those of Fownes being in the case of  $75.75$  according to Squibb, which is  $76.0$  p.c. according

to Fownes. The more dehydrated alcohol of Squibb accounts for  $\cdot 1$  p.c. of this  $\cdot 25$ , so that no greater difference of observation than  $\cdot 18$  p.c. is to be found in the work of these three authorities. The results of Tralles' and Gay-Lussac's experiments, being based upon a less dehydrated alcohol, do not compare so precisely with those of Fownes, but the discrepancy never exceeds  $\cdot 4$  p.c.

Specific gravity	Per-centage of alcohol	Specific gravity	Per-centage of alcohol	Specific gravity	Per-centage of alcohol
$\cdot 9991$	0.5	$\cdot 9511$	34	$\cdot 8769$	68
$\cdot 9981$	1	$\cdot 9490$	35	$\cdot 8745$	69
$\cdot 9965$	2	$\cdot 9470$	36	$\cdot 8721$	70
$\cdot 9947$	3	$\cdot 9452$	37	$\cdot 8696$	71
$\cdot 9930$	4	$\cdot 9434$	38	$\cdot 8672$	72
$\cdot 9914$	5	$\cdot 9416$	39	$\cdot 8649$	73
$\cdot 9898$	6	$\cdot 9396$	40	$\cdot 8625$	74
$\cdot 9884$	7	$\cdot 9376$	41	$\cdot 8603$	75
$\cdot 9869$	8	$\cdot 9356$	42	$\cdot 8581$	76
$\cdot 9855$	9	$\cdot 9335$	43	$\cdot 8557$	77
$\cdot 9841$	10	$\cdot 9314$	44	$\cdot 8533$	78
$\cdot 9828$	11	$\cdot 9292$	45	$\cdot 8508$	79
$\cdot 9815$	12	$\cdot 9270$	46	$\cdot 8483$	80
$\cdot 9802$	13	$\cdot 9249$	47	$\cdot 8459$	81
$\cdot 9789$	14	$\cdot 9228$	48	$\cdot 8434$	82
$\cdot 9778$	15	$\cdot 9206$	49	$\cdot 8408$	83
$\cdot 9766$	16	$\cdot 9184$	50	$\cdot 8382$	84
$\cdot 9753$	17	$\cdot 9160$	51	$\cdot 8357$	85
$\cdot 9741$	18	$\cdot 9135$	52	$\cdot 8331$	86
$\cdot 9728$	19	$\cdot 9113$	53	$\cdot 8305$	87
$\cdot 9716$	20	$\cdot 9090$	54	$\cdot 8279$	88
$\cdot 9704$	21	$\cdot 9069$	55	$\cdot 8254$	89
$\cdot 9691$	22	$\cdot 9047$	56	$\cdot 8228$	90
$\cdot 9678$	23	$\cdot 9025$	57	$\cdot 8199$	91
$\cdot 9665$	24	$\cdot 9001$	58	$\cdot 8172$	92
$\cdot 9652$	25	$\cdot 8979$	59	$\cdot 8145$	93
$\cdot 9638$	26	$\cdot 8956$	60	$\cdot 8118$	94
$\cdot 9623$	27	$\cdot 8932$	61	$\cdot 8089$	95
$\cdot 9609$	28	$\cdot 8908$	62	$\cdot 8061$	96
$\cdot 9593$	29	$\cdot 8886$	63	$\cdot 8031$	97
$\cdot 9578$	30	$\cdot 8863$	64	$\cdot 8001$	98
$\cdot 9560$	31	$\cdot 8840$	65	$\cdot 7969$	99
$\cdot 9544$	32	$\cdot 8816$	66	$\cdot 7938$	100
$\cdot 9528$	33	$\cdot 8793$	67		

In the assessment of duty and in commercial transactions in this country the standard of strength is called 'proof.' This standard has been found to have the specific gravity of

$\cdot 91984$  at  $\frac{15.6^\circ}{15.6^\circ}$ , and to contain 49.24 p.c. by weight of alcohol of the specific gravity of  $\cdot 79381$ , and by measure 57.06 p.c. It should be understood, however, that in speaking of 57.06 p.c. by measure, we mean that 100 gallons of this proof spirit contains 57.06 gallons of alcohol. If this alcohol were separated from the water, it would be found that 57.06 gallons of alcohol and 46.68 gallons of water would be produced—a total of 103.74 gallons; and if these proportions of alcohol and water were mixed again, they would be found to have contracted in measure to 100 gallons.

The hydrometer of Sikes, being the legalised instrument of the Revenue in Great Britain and Ireland as well as of most of the British colonies, is generally adopted in commerce for estimating the strength of spirits. It is made of hard

metal, gilded, and consists of a hollow ball, into one end of which a stem is inserted, and into the other end a thin solid cylinder, ending in a knob. The stem is marked 10 at the lower and 0 at the upper end, and between these two extremes there is a mark for every  $\frac{2}{10}$ ths, each division being equal in length. When the instrument, on being placed in spirit at the temperature of 15·6°, rises to 0, it represents a strength of 67 overproof, or 95·3 per cent. of the alcohol of Tralles; and when it sinks to 10 it represents 58·2 overproof, or 90·2 per cent. of the same alcohol. For strengths weaker than these nine weights are employed, the smallest being marked 10 and the largest and heaviest 90. These are attached to the knob at the lower end of the instrument. When the stem sinks to 10 with the 90 weight attached, at the temperature of 10·6°, the indication is 100, representing distilled



water. The indications are interpreted in actual strength overproof and underproof by means of a book of tables which accompanies the instrument. The results are accurate at the temperature at which the instrument has been adjusted, and between 5·5° (42°F.) and 20° (68°F.) it does not show any greater error than ·5 p.c. of alcohol. It possesses an advantage over most other alcoholometers in the fact that its scale can be easily read to ·2 p.c. of alcohol.

On the Continent the alcoholometers of Gay-Lussac and of Tralles are those most extensively used. They are made of glass, are without weights, and differ from the hydrometer of Sikes in indicating, the first at a temperature of 15° and the second at 15·6°, the percentage of alcohol by measure, without reference to any table. The differences in their results are so slight as to permit of the instruments being interchangeable for commercial purposes, but their scales are not marked for less than 1 p.c. of alcohol. The National Academy of Sciences of the United States (Senate Mis. Doc. 44, 1867) have recommended the adoption of a series of five of these alcoholometers, each having a limited range, and the scales being proportionately larger. On the other hand, the Russian Government in 1872 permitted the use, side by side with the alcoholometer of Tralles, of a metal instrument, resembling that of Sikes in form and in the number of its weights, but reversing the indications of Sikes, so that 100 is made to represent 95·5 p.c. of Tralles' alcohol at 15·6°, and 0 to represent water.

By means of Table I. the indications of any one of these instruments can be converted into degrees of any other, into percentages of alcohol by measure, or into English or American proof at the temperature of 15·6° (60°F.). The column marked percentage of alcohol of France refers to the alcoholometers of Gay-Lussac, of Tralles, and of Meissner.

The hydrometers of Cartier and Baumé are still to some extent used in France, and that of Beck in Switzerland.

An example will best show how to use the table. Let the Gay-Lussac or Tralles alcoholometer show 86 p.c. of alcohol at 10° (50°F.) or 5·6° (10°F.) below the standard of 15·6° (60°F.). The specific gravity corresponding to 86 p.c. in the table of strengths (Table I.) is ·8466. The correction for each degree of centigrade temperature between ·8100 and ·8500 in Table II. is ·00085 which multiplied by 5·6 produces ·0047. The temperature being below the standard, ·0047 must be *deducted* from the specific gravity. Therefore ·8466 - ·0047 = ·8419, and this specific gravity in Table I. will be found to correspond very nearly to 87·7 p.c. of alcohol or 53·7 English overproof. If the 86 p.c. of alcohol had been found at 21·2° (70°F.) the figures ·0047 must be *added* to ·8466, producing ·8513, equal to very nearly 84·2 p.c. of alcohol.

In comparing American with English proof, it is necessary to remember that the American gallon is smaller than the English imperial gallon, 100 English being equal to 120 American gallons. After allowing for this difference it will be found that 100 English *proof* gallons are equal to 136·95 American *proof* gallons.

Up to the year 1881, the strength of brandy and rum was for the purposes of duty assumed to be that indicated by Sikes' hydrometer, irrespective of the amount of solid matter which they might contain. By a clause in the 44 Vict. c. 12 it was provided that the amount by which the real strength was obscured should be added to the strength indicated by the hydrometer. The duty is, therefore, now levied on the actual amount of alcohol contained in the liquid. This is generally ascertained by distilling about three-fourths of a given bulk, making the distillate up to the original bulk with water, and taking the strength of this liquid to be the strength of the spirit. The same process is adopted for estimating the amount of spirit in liqueurs and in wines. Another method is to evaporate a given weight to dryness in a water-oven, weigh the dry solid matter and calculate its percentage on the given weight. This percentage multiplied by factors, which increase from 2·2 for 40 overproof to 3·8 for 30 underproof, gives the degrees of proof spirit to be added to the apparent strength in order to find the real strength on English proof.

Many methods have been described for the purpose of registering the quantity and strength of spirits passing from the still to the receiver at stilleries. A very ingenious apparatus, and one extensively used on the Continent, is that of Siemens. It consists of three vessels. In the first the spirit is mixed. The second contains a large float which, acting on a spring, indicates the strength of the spirit. The third is a large drum divided into three sections, and containing a smaller drum round its axis. The spirit passes from the second vessel into the smaller drum, and from thence into that section of the larger drum the position of which is vertical to the axis. This section continues in a vertical position until it is filled, after which the spirit rises in the smaller drum to a point at which it runs into the section next adjoining that which had been filled. This causes the filled section to tilt and empty itself. Each emptying is registered, and the capacity of each section known.

TABLE I.

Specific gravity	Indication of Sikes' hydrometer	Percentage volume of			Indication of hydrometer of		
		English proof	American proof	Alcohol of France, Germany, Belgium, Sweden, Austria, and Russia	Baumé	Cartier	Beck
		Overproof					
·7946	—	75·2	200	100	47°	—	44
·7995	—	73·1	198	99	46	—	42·5
·8041	—	71·3	196	98	45	—	40·8
·8084	—	69·6	194	97	44	—	40
·8125	—	68·0	192	96	43	—	39
·8152	0	67·0	190·6	95·3	—	—	—
·8164	—	66·6	190	95	—	—	38
·8171	1	66·1	189·6	94·8	42	—	—
·8189	2	65·3	188·6	94·3	—	—	—
·8201	—	64·8	188	94	—	—	—
·8206	3	64·5	187·6	93·8	—	—	37
·8225	4	63·6	186·6	93·3	—	—	—
·8237	—	63·0	186	93	41	—	—
·8244	5	62·7	185·6	92·8	—	—	36
·8262	6	61·8	184·6	92·3	—	—	—
·8272	—	61·2	184	92	40	—	—
·8280	7	60·9	183·6	91·8	—	39	—
·8298	8	60·0	182·6	91·3	—	—	35
·8306	—	59·4	182	91	—	—	—
·8315	9	59·1	181·4	90·7	39	—	—
·8332	10	58·2	180·4	90·2	—	38	34
·8340	—	57·8	180	90	—	—	—
·8349	11	57·3	179·4	89·7	—	—	—
·8366	12	56·4	178·4	89·2	—	—	—
·8373	—	56·0	178	89	38	—	33
·8383	13	55·5	177·4	88·7	—	37	—
·8399	14	54·6	176·4	88·2	—	—	—
·8405	—	54·3	176	88	—	—	—
·8415	15	53·8	175·4	87·7	37	—	32
·8433	16	52·7	174·2	87·1	—	36	—
·8436	—	52·6	174	87	—	—	—
·8450	17	51·8	173	86·5	—	—	31
·8466	—	50·8	172	86	—	—	—
·8468	18	50·7	172	86	36	35	—
·8485	19	49·7	170·8	85·4	—	—	—
·8496	—	49·1	170	85	—	—	—
·8502	20	48·7	169·6	84·8	—	—	30
·8520	21	47·6	168·2	84·1	35	34	—
·8526	—	47·4	168	84	—	—	—
·8537	22	46·6	167·2	83·6	—	—	29
·8553	23	45·6	166	83	—	—	—
·8555	—	45·6	166	83	—	—	—
·8570	24	44·6	165	82·5	34	33	—
·8583	—	43·7	164	82	—	—	28
·8587	25	43·5	163·8	81·9	—	—	—
·8605	26	42·4	162·4	81·2	—	—	—
·8611	—	42·1	162	81	33	32	—
·8622	27	41·3	161·2	80·6	—	—	27
·8639	28	40·2	160	80	—	—	—
·8657	29	39·1	158·6	79·3	—	—	—
·8664	—	38·7	158	79	32	31	—
·8674	30	38·0	157·4	78·7	—	—	26
·8691	31	36·9	156·2	78·1	—	—	—
·8693	—	36·9	156	78	—	—	—
·8709	32	35·7	154·8	77·4	—	—	—
·8720	—	35·0	154	77	31	—	25
·8728	33	34·5	153·4	76·7	—	—	—
·8745	—	33·4	152·2	76·1	—	30	—
·8747	—	33·3	152	76	—	—	—
·8762	35	32·2	150·8	75·4	—	—	24



TABLE I.—*continued.*

Specific gravity	Indication of Sikes' hydrometer	Percentage volume of			Indication of hydrometer of		
		English proof	American proof	Alcohol of France, Germany, Belgium, Sweden, Austria, and Russia	Baumé	Cartier	Beck
		Overproof					
·8773	—	31·5	150	75	30	—	—
·8780	35	31·0	149·4	74·7	—	—	—
·8798	37	29·8	118	74·0	—	29	—
·8817	33	28·5	116·6	73·3	—	—	23
·8821	—	28·0	116	73	—	—	—
·8835	39	27·3	115·2	72·6	29	—	—
·8850	—	26·2	114	72	—	28	—
·8851	40	26·0	113·8	71·9	—	—	22
·8871	41	24·8	112·4	71·2	—	—	—
·8875	—	21·1	112	71	—	—	—
·8890	42	23·5	119·8	70·4	23	—	—
·8900	—	22·8	119	70	—	27	21
·8908	43	22·2	139·1	69·7	—	—	—
·8926	41	20·9	138	69	—	—	—
·8945	45	19·6	136·4	68·2	27	—	—
·8949	—	19·2	135	68	—	26	20
·8962	46	18·3	135	67·5	—	—	—
·8973	—	17·5	134	67	—	—	—
·8982	47	16·9	133·4	66·7	—	—	—
·8997	—	15·8	132	65	26	—	19
·8999	43	15·6	131·8	65·9	—	—	—
·9018	49	11·2	130·2	65·1	—	25	—
·9021	—	11·0	130	65	—	—	—
·9036	50	12·8	128·6	64·3	—	—	—
·9041	—	12·3	123	64	—	—	18
·9055	51	11·4	127	63·5	25	—	—
·9067	—	10·5	126	63	—	—	—
·9073	52	10·0	125·1	62·7	—	24	—
·9091	53	8·6	124	62	—	—	17
·9110	51	7·1	122·2	61·1	—	—	—
·9112	—	7·0	122	61	24	—	—
·9129	—	5·6	120·4	60·2	—	—	—
·9131	—	5·5	120	60	—	—	13
·9147	56	4·2	118·8	59·4	—	23	—
·9156	—	3·7	118	59	—	—	—
·9166	57	2·7	117·2	58·6	23	—	—
·9178	—	1·8	116	58	—	—	—
·9183	58	1·4	115·6	57·8	—	—	15
·91981	—	Proof	111·6	57·3	—	—	—
		Underproof					
·9293	59	0·3	113·8	56·9	—	22	—
·9222	60	1·9	112	56	22	—	—
·9249	61	3·4	110·2	55·1	—	—	14
·9242	—	3·5	110	55	—	—	—
·9259	62	5·0	108·4	51·2	—	—	—
·9252	—	5·1	108	54	—	21	—
·9279	63	6·7	106·4	53·2	—	—	—
·9283	—	7·0	106	53	21	—	13
·9298	64	8·3	104·6	52·3	—	—	—
·9303	—	8·7	104	52	—	—	—
·9317	65	10·0	102·8	51·4	—	—	—
·9323	—	10·6	102	51	—	—	—
·9336	66	11·7	100·8	50·4	—	20	—
·9313	—	12·4	100	50	20	—	12
·9358	67	13·5	98·6	49·3	—	—	—
·9362	—	13·9	98	49	—	—	—
·9375	63	15·3	96·6	48·3	—	—	—
·9381	—	15·8	96	48	—	—	—
·9391	69	17·3	94·6	47·3	—	—	11

TABLE I.—*continued.*

Specific gravity	Indication of Sikes' hydrometer	Percentage volume of			Indication of hydrometer of		
		English proof	American proof	Alcohol of France, Germany, Belgium, Sweden, Austria, and Russia	Baumé	Cartier	Beck
		Underproof					
·9399	—	17·6	94	47	—	—	—
·9413	70	18·8	92·6	46·3	—	19	—
·9417	—	19·2	92	46	19	—	—
·9432	71	20·8	90·4	45·2	—	—	—
·9435	—	21·1	90	45	—	—	—
·9451	72	22·7	88·2	44·1	—	—	10
·9452	—	22·8	88	44	—	—	—
·9470	73	24·7	86	43	18	18	—
·9487	—	26·4	84	42	—	—	—
·9489	74	26·7	83·6	41·8	—	—	9
·9503	—	28·0	82	41	—	—	—
·9509	75	28·8	81·2	40·6	—	—	—
·9519	—	29·9	80	40	—	—	—
·9528	76	31·0	78·8	39·4	—	—	—
·9535	—	31·8	78	39	17	—	—
·9548	77	33·1	76·2	38·1	—	—	8
·9550	—	33·3	76	38	—	17	—
·9565	—	35·2	74	37	—	—	—
·9567	78	35·6	73·6	36·8	—	—	—
·9579	—	36·8	72	36	—	—	—
·9587	79	33·1	70·6	35·3	—	—	—
·9592	—	38·7	70	35	16	—	—
·9605	—	40·3	68	34	—	—	—
·9606	80	40·5	67·8	33·9	—	—	7
·9618	—	42·4	66	33	—	—	—
·9625	81	43·3	64·8	32·4	—	16	—
·9631	—	44·1	64	32	—	—	—
·9643	—	45·8	62	31	—	—	—
·9645	82	46·1	61·6	30·8	—	—	—
·9655	—	47·5	60	30	—	—	6
·9666	83	49·1	58	29	15	—	—
·9677	—	50·9	56	28	—	—	—
·9684	84	52·2	54·6	27·3	—	—	—
·9688	—	52·7	54	27	—	—	—
·9698	—	54·5	52	26	—	15	—
·9704	85	55·5	50·8	25·4	—	—	—
·9709	—	56·3	50	25	—	—	—
·9719	—	57·9	48	24	—	—	5
·9725	86	59·0	46·2	23·1	—	—	—
·9729	—	59·3	46	23	14	—	—
·9740	—	61·4	44	22	—	—	—
·9745	87	62·5	42·8	21·4	—	—	—
·9750	—	63·2	42	21	—	—	—
·9760	—	65·0	40	20	—	—	—
·9766	88	66·0	38·8	19·4	—	14	—
·9770	—	66·7	38	19	—	—	4
·9780	—	68·6	36	18	—	—	—
·9785	89	69·4	35	17·5	—	—	—
·9790	—	70·3	34	17	13	—	—
·9800	—	72·0	32	16	—	—	—
·9805	90	72·8	31	15·5	—	—	—
·9811	—	73·7	30	15	—	—	—
·9821	—	75·4	28	14	—	—	—
·9826	91	76·1	27·2	13·6	—	—	3
·9832	—	77·0	26	13	—	—	—
·9844	—	79·1	24	12	—	13	—
·9845	92	79·2	23·8	11·9	—	—	—
·9854	—	80·6	22	11	—	—	—
·9865	93	82·3	20	10	12	—	—
·9878	—	83·9	18	9	—	—	—

TABLE I. — *continued.*

Specific gravity	Indication of Sikes' hydrometer	Percentage volume of			Indication of hydrometer of		
		English proof	American proof	Alcohol of France, Germany, Belgium, Sweden, Austria, and Russia	Baumé	Cartier	Beck
·9886	94	Underproof	85·2	16·6	8·3	—	2
·9890	—	85·8	16	8	—	—	—
·9902	—	87·8	14	7	—	—	—
·9904	95	88·0	13·8	6·9	—	—	—
·9915	—	89·6	12	6	—	12	—
·9925	96	90·7	10·6	5·3	—	—	—
·9928	—	91·2	10	5	11	—	—
·9942	—	93·0	8	4	—	—	—
·9944	97	93·3	7·6	3·8	—	—	1
·9956	—	94·7	6	3	—	—	—
·9965	98	95·9	4·6	2·3	—	—	—
·9970	—	96·5	4	2	—	—	—
·9985	99	98·2	2	1	—	—	—
1000·0	—	Water	—	—	10	11	0

Between the temperature of 4° and 78·8° water increases in bulk to the extent of 2·8 per cent. Alcohol within the same degrees increases very nearly 9 per cent. Silberman (C. R. 27, 418) has taken advantage of this difference in the rate of expansion of alcohol and water in order to determine the strength of spirits. A thermometer is filled up to a certain mark with the spirit at 25°, and after the liquid has been exhausted of air an observation is made of the amount by which it expands when heated to 50°. The percentage of alcohol is found by means of a scale graduated by direct observation upon a number of samples of known strength.

The results shown in Table I. are only true at 15·6° (60°F.), but the indications at any other temperature may be approximately

converted into those of the table by making the following corrections for temperature:—

TABLE II.

Spec. gravities	Correction for each degree Centigrade	Correction for each degree of F.
·8100 to ·8500	·00085	·00047
·8500 to ·8900	·00083	·00046
·8900 to ·9200	·00080	·00044
·9200 to ·9400	·00075	·00042
·9400 to ·9500	·00069	·00038
·9500 to ·9600	·00060	·00033
·9600 to ·9700	·00044	·00024
·9700 to ·9800	·00026	·00014
·9800 to ·9900	·00016	·00009

TABLE III.—SHOWING THE QUANTITY OF WATER REQUIRED TO REDUCE 100 VOLUMES OF A STRONGER SPIRIT TO A SPIRIT OF LOWER STRENGTH.

	90	85	80	75	70	65	60	55	50
85	6·56								
80	13·79	6·83							
75	21·89	14·48	7·20						
70	31·05	23·14	15·35	7·64					
65	41·53	33·03	24·66	16·37	8·15				
60	53·65	44·48	35·44	26·47	17·58	8·76			
55	67·87	57·90	48·67	38·52	28·63	19·02	9·47		
50	84·71	73·90	63·04	52·43	41·73	31·25	20·47	10·35	
45	105·34	93·30	81·38	69·54	57·78	46·09	34·46	22·90	11·41
40	130·80	117·34	104·01	90·76	77·58	64·48	51·43	38·46	25·55
35	163·28	148·01	132·88	117·82	102·84	87·93	73·08	58·31	43·59
30	206·22	188·57	171·05	103·53	136·04	118·94	101·71	84·54	67·45
25	266·12	245·15	224·30	253·61	182·83	162·21	141·65	121·16	100·73
20	355·80	329·84	304·01	278·26	252·58	226·98	201·43	175·96	150·55
15	505·27	471·00	436·85	402·81	368·83	334·91	301·07	267·29	233·64
10	804·54	753·63	702·89	651·21	601·60	551·06	500·59	450·19	399·85

The original percentages by volume of alcohol are here placed at the head of the columns, and the percentages to which they are required to be reduced in the first column of the table. G. N. S.



**ALDEHYDE** *Acetaldehyde*  $C_2H_4O$  or  $CH_3\cdot COH$ . A product of the oxidation of ordinary (ethylic) alcohol. Aldehyde occurs, together with its polymerides metaldehyde and paraldehyde, in the 'first runnings' from the stills in the rectification of alcohol which has been filtered through charcoal (Krämer and Pinner, B. 2, 403; 4, 787); the best yield is obtained from the alcohol manufactured from potatoes and from the sugar beet. It is also present in crude wood spirit (Krämer and Grodzki, B. 9, 1921). Aldehyde is also formed when calcium formate is heated with calcium acetate (Limpricht, A. 97, 369), and when lactic acid and the lactates are distilled with manganese dioxide and sulphuric acid (Städeler, A. 69, 333); it is also one of the products of the dry distillation of sugar (Völckel, A. 87, 303).

*Preparation.*—Aldehyde is formed by the oxidation of alcohol by means of platinum black (Döbereiner, Gm. 8, 274), of manganese dioxide and sulphuric acid (Liebig, A. 14, 133), or of potassium dichromate and sulphuric acid (Städeler, J. 1859, 329). When prepared by Liebig's method, 2 parts of 80 p.c. alcohol are heated with 3 parts of manganese dioxide, 3 parts of sulphuric acid and 2 parts of water, and the distillation carried on until the distillate begins to show an acid reaction; this point is reached when about three parts have collected in the well-cooled receiver. The distillate containing alcohol, acetal and ethereal salts is then distilled with an equal weight of calcium chloride, and  $1\frac{1}{2}$  parts collected; this is again rectified with an equal weight of calcium chloride and  $\frac{3}{4}$  part distilled over. The product so obtained is nearly anhydrous, but still contains alcohol and small quantities of ethereal salts; to free it from these, it is dissolved in 2 vols. of ether, saturated with ammonia in the cold, and the aldehyde-ammonia which separates is collected, dissolved in water, distilled with dilute sulphuric acid in a water-bath, and the distillate rendered anhydrous by rectification over calcium chloride at as low a temperature as possible.

Commercially, aldehyde is obtained from the 'first runnings' of the alcohol stills. A special form of still in which the separation of aldehyde from alcohol is brought about during the rectification of the latter is figured and described by Galland (D. P. J. 259, 225).

*Properties.*—Aldehyde is a colourless liquid having an extremely pungent suffocating odour; it is very inflammable, and burns with a feebly luminous flame. Its b.p. =  $20\cdot8^\circ$ , and sp.gr. =  $0\cdot80092$  at  $0^\circ$  (Kopp, A. 64, 214); its sp.gr. =  $0\cdot79509$  at  $10^\circ$ , =  $0\cdot79138$  at  $13^\circ$ , =  $0\cdot78761$  at  $16^\circ$  (Perkin, C. J. 45, 475). It is soluble in all proportions in alcohol, ether and water, and is separated from the aqueous solution as an ethereal layer on addition of calcium chloride. When heated with aqueous soda or potash, so-called aldehyde resin is obtained as a brown mass (Liebig, *loc. cit.*; Weidenbusch, A. 66, 153). Sodium amalgam converts aldehyde into ethylic alcohol, a small quantity of  $\beta$ -butyleneglycol being formed simultaneously (Kekulé, A. 162, 310); whilst phosphorus pentachloride reacts with it yielding ethylidene dichloride (Geuther, A. 105, 323).

Aldehyde readily polymerises in the presence of small quantities of various substances, such as sulphuric acid, phosgene, zinc chloride, hydrogen chloride, sulphur dioxide, &c., and two compounds are obtained whose relative quantities depend upon the temperature; the chief product being metaldehyde ( $C_4H_8O_4$ ) (Hanriot and Oeconomides, A. Ch. [5] 25, 227), when the action takes place in a freezing mixture, and the isomeric paraldehyde (elaldehyde) when it occurs at the ordinary temperature (Kekulé and Zincke, A. 162, 125). *Paraldehyde* is a colourless liquid, crystallising below  $10^\circ$  in large transparent prisms; its b.p. =  $124^\circ$  at 759·8 mm. and sp.gr. =  $0\cdot998$  at  $15^\circ$  (Kekulé and Zincke); sp.gr. =  $0\cdot99925$  at  $15^\circ$  (Perkin, C. J. 45, 479); b.p. =  $123\cdot2^\circ$ – $123\cdot5^\circ$  at 744 mm. (Brühl, A. 203, 26). *Metaldehyde* crystallises in needles or tetragonal prisms, sublimes without previous fusion at  $112^\circ$ – $115^\circ$ , and when heated in sealed tubes at  $120^\circ$  is entirely reconverted into ordinary aldehyde. Neither polymeride is resinised by aqueous soda or potash, but in other reactions they behave generally as ordinary aldehyde and yield similar products (Kekulé and Zincke).

*Reactions.*—Aldehyde in aqueous solution very readily reduces an ammoniacal solution of silver nitrate giving a bright metallic mirror. Acetaldehyde (and all aldehydes which are stable in aqueous soda solution) can be detected by adding to a solution of the suspected substance in dilute alkali a fresh solution of 1 part of paradiabenzene-sulphonic acid in 60 parts of water rendered alkaline with a little soda, and then some sodium amalgam; if an aldehyde is present, a reddish-brown colour is developed after the mixture has stood for 10–20 minutes (Penzoldt and Fischer, B. 16, 657).

Aldehyde very readily yields condensation compounds; thus, when allowed to remain in the cold with dilute hydrochloric acid, or with aqueous solutions of zinc chloride or of salts having an alkaline reaction, such as potassium carbonate, aldol is obtained, whilst crotonaldehyde is formed when it is heated with concentrated hydrochloric acid (Kekulé, A. 162, 92).

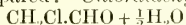
*Additive compounds.*—Aldehyde not only shows a strong tendency to yield polymerides and condensation compounds, but unites directly with a large number of substances.

- (1) Compounds with alcohols:—*v.* ACETAL.
- (2) Compounds with acids:—(Geuther, A. 106, 249; Lieben, A. 106, 336; 178, 43; Rübenkamp, A. 225, 279; Schiff, B. 9, 304).
- (3) Compounds with alkaline sulphites:—Aldehyde forms definite crystalline compounds when dissolved in concentrated aqueous solutions of the acid sulphites (bisulphites) of the alkali metals. The *potassium* salt,  $C_2H_4O\cdot KHSO_3$ , crystallises in indistinct needles; the *sodium* salt,  $C_2H_4O\cdot NaHSO_3 + \frac{1}{2}H_2O$ , in fine needles or nacreous plates; but the ammonium compound has the formula  $C_2H_4(OH)SO_3\cdot NH_4$ . These salts are almost insoluble in excess of the sulphite, and separate in the crystalline state; from them aldehyde can be obtained by distillation with a stronger acid or an alkaline carbonate (Bunte, A. 170, 305).
- (4) Compound with ammonia:—*Aldehyde-ammonia*,  $C_2H_4O\cdot NH_3$ , obtained by leading dry ammonia into aldehyde in ethereal solution

(Liebig, A. 14, 144), crystallises in large rhombohedra, melts at 70°–80°, boils at 100° without decomposition, and is decomposed into its constituents on distillation with dilute acids.

(5) Compounds with hydrocyanic acid:—(Tiemann, B. 14, 1965; Strecker, A. 91, 349; Erlenmeyer and Passavant, A. 200, 120).

**Substitution-derivatives.**—The action of chlorine on aldehyde has been studied by Wurtz (A. 102, 93), Wurtz and Voigt (Bl. 17, 402), and by Pinner (A. 179, 21). Pinner finds that when chlorine is passed into ordinary aldehyde at 10°, metaldehyde and paraldehyde are first formed, and these subsequently yield substitution-derivatives, of which chloral is the chief product, butyric chloral and dichloraldehyde being formed in smaller quantity. The following derivatives have been prepared:—*Chloraldehyde*,



(Natterer, M. 3, 446); *dichloraldehyde*,  $\text{CHCl}_2.\text{CHO}$  (Grimaux and Adams, Bl. 34, 29); *trichloraldehyde* (v. CHLORAL).

The bromine derivatives have been examined by Pinner (B. 7, 1499, and *lc.*).

**ALDEHYDES.** The name aldehyde, originally assigned to the compound obtained by the limited oxidation of ethylic alcohol, has come to possess a wider signification, and is now used as a generic term for a class of organic substances which are similarly derived from the primary alcohols. In composition the aldehydes differ from the alcohols from which they are derived by containing two atoms of hydrogen fewer in the molecule; whilst in their chemical behaviour they all exhibit the general properties of the typical member of the series, acetaldehyde.

**ALDEHYDINE v. BONE OIL.**

**ALDEHYDINES.** Compounds formed by the condensation of ortho-diamines with aldehydes (Ladenburg, B. 10, 1126).

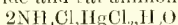
**ALDER BARK.** *Aune*, Fr.; *Erle*, Ger.; *Alnus glutinosa*, L. Used for tanning and dyeing. The percentage of tannin varies from 16 to 18 (Eitner, Zeit. f.d. chem. Grossgew. 3, 668; 1, 279).

Lamasse states that the tannin is a methyl tannin like that of the oak, that it gives a reddish-blue precipitate with ferrous acetate, an olive-green precipitate with ferrous sulphate, and is precipitated by a gum solution.

A solution of the bark is employed for obtaining black, greys, and browns on linen; in Germany for reds, and in Kamtschatka for colouring skins a red tint (Girardin's Chemie, 4, 360).

**ALE v. BREWING.**

**ALEMBROTH, SALT OF.** A compound of mercuric chloride and sal ammoniac



formed by mixing the two salts in molecular proportions. Also called by the alchemists Salt of Wisdom.

**ALFA v. HALFA.**

**ALGÆ.** *Vareeh* or *Algues*, Fr.; *Tange Seegras* or *Algen*, Ger. A class of cryptogamous plants including the seaweeds and the lavers growing in sea-water, and the fresh-water confervæ. Many of the salt-water species are edible, none of them is poisonous.

*Rhodomenia palmata* (dulse, dylish or delish) and *Alaria esculenta* (murlins) are used

as food by the peasantry of the Highlands and of Ireland. *Porphyra laciniata* (laciniated purple laver), very abundant on the British coasts, is sold in England as laver, in Ireland as sloke, and in Scotland as slaak. *Chondrus crispus* (carrageen, Irish or pearl moss) is collected on the west coast of Ireland, and is frequently used there by painters and plasterers as a substitute for size. It is also used in making jellies, &c., in medicine; and a thick mucilage scented with some prepared spirit is sold as 'bandolin,' 'fixature,' or 'clysphitique,' and is employed for stiffening silks.

Amongst other algae having an economic value are Ceylon moss or edible moss (*Gracilaria lichenoides*), found in the Indian archipelago; the agar-agar of Malacca, or agal-agal of China, which is derived from *Gracilaria lichenoides*, *Eucheuma spinosum* and probably other algae. The substance is now much used in bacteriological research as a nutrient jelly; for gumming silks, paper, &c., and for making a paste not liable to be eaten by insects.

Manna, or mannite, can be obtained from *Laminaria saccharina* or sugar wrack, found on sandy shores attached to pebbles.

The following table shows the composition of various species of algae; the quantity of nitrogen in some of them is remarkably large.

Alga	Water	Dry matter	Per cent. nitrogen in dry matter	Protein contained in dry matter
<i>Chondrus crispus</i> , bleached from Bewlay Evans	17.92	82.08	1.531	9.587
<i>Chondrus crispus</i> , bleached second experiment	19.79	80.21	1.185	9.281
<i>Chondrus crispus</i> , unbleached, Ballycastle	21.47	78.53	2.142	13.387
<i>Chondrus crispus</i> , unbleached, second experiment	19.96	80.04	2.510	15.687
<i>Gigartina mamillata</i> , Ballycastle	21.55	78.45	2.198	13.737
<i>Laminaria digitata</i> , or dulse tangle	21.38	78.62	1.588	9.925
<i>Rhodomenia palmata</i>	16.56	83.44	3.465	21.656
<i>Porphyra laciniata</i>	17.41	82.59	4.670	29.062
<i>Sarcophyllis edulis</i>	19.61	80.39	3.088	19.300
<i>Alaria esculenta</i>	17.91	80.09	2.424	15.150

**ALGAROTH, POWDER OF.** *Powder of Algarotti, English Powder.* A crystalline oxychloride of antimony, obtained by pouring antimony chloride into hot water. Used in the preparation of tartar emetic.

**ALGAROVILLA.** The fruit of the *Prosopis pallida* *Juga Marthæ*, of Santa Martha, in the province of New Carthage. The pods contain large quantities of tannin, and hence are used for tanning leather. Algarovilla is said to possess more than four times the power of good oak bark.

**ALGIN.** A nitrogenous body obtained from seaweed, somewhat resembling albumen (v. IODINE).

**ALHAGI MAURORUM, JAWASA or TARRANJABIN.** An Indian drug, from a species of leguminosæ, used for rheumatism; it is a laxative and diuretic (Ph. [3] 9, 145).



**ALIZARIN AND ALLIED COLOURING MATTERS.** Madder, *Rubia tinctoria*, which was for a very long time used on a very large scale in the 'Turkey-Red' industry, contains two colouring matters, alizarin and purpurin, of which the former is by far the most important.

Alizarin is not found ready-formed in the madder-root, but exists there in the form of a glucoside called 'rubianic acid' which when allowed to ferment, or when boiled with dilute acid, splits up readily into alizarin and glucose.

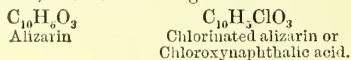
The colouring matter itself was first isolated from the madder-root in 1827, by Colin and Robiquet, who obtained it by extracting ground madder with hot water and subliming the purified extract carefully in a glass tube.

This method of sublimation was not considered sufficient proof of the existence of alizarin in madder, and it was not till Dr. Schunck succeeded in isolating this substance by chemical means from the madder extracts used by dyers that this important point was definitely settled.

In assigning the correct formula to alizarin, considerable difference of opinion existed at first, owing no doubt to some extent to the difficulty experienced in obtaining alizarin in a condition pure enough for accurate analysis.

Schunck proposed the formula  $C_{11}H_{10}O_4$ , whilst Strecker believed it to be  $C_{10}H_8O_3$  and related to 'chloroxynaphthalic acid' (chlorohydroxynaphthaquinone), a derivative of naphthalene, since both these substances on oxidation yield phthalic acid.

Strecker's formula was the more generally accepted by chemists, and chloroxynaphthalic acid was looked upon as being simply chlorinated alizarin, the two bodies being thus related:—



In order to prove the relation supposed to exist between these two substances it was only necessary to replace the chlorine atom in chloroxynaphthalic acid by hydrogen, when alizarin would result.

This operation was eventually accomplished by Martius and Griess who obtained thus a substance of the formula  $C_{10}H_8O_3$ , which was, however, not identical with alizarin, and was therefore supposed to be isomeric with it.

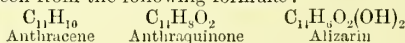
Some time after these experiments of Martius and Griess, Graebe commenced his research on quinones, the working out of which led not only to results which proved beyond a doubt what the chemical nature of alizarin really was, but also eventually resulted in the artificial production of this important colouring matter. In pursuing this investigation Graebe succeeded in preparing chloranil  $C_6Cl_4O_2$ , by treating phenol with potassium chlorate and hydrochloric acid, and in acting on this with caustic potash he found that two of the atoms of chlorine in this compound became replaced by (OK), producing the potash salt of chloranilic acid  $C_6Cl_2(OK)_2O_2$ , a change the knowledge of which proved to be of the utmost importance in his subsequent experiments on the artificial production of alizarin.

Chloroxynaphthalic acid was now considered by Graebe to be related to naphthalin in much

the same way as chloranil was to benzene, i.e. to be a derivative of naphthaquinone.

Soon after this the attention of Graebe, in conjunction with that of Liebermann, was turned to alizarin, which they also thought might belong to the quinone series.

In determining the constitution of this substance, the first step necessary was to obtain some information as to the nature of the hydrocarbon from which alizarin was derived and this was done in the following way: Alizarin prepared from madder was mixed with zinc-dust and heated strongly in a furnace, according to Baeyer's method of reducing benzenoid compounds, and in this way a crystalline hydrocarbon was obtained having the composition  $C_{11}H_{10}$  which on examination was found to be identical with anthracene, a hydrocarbon previously obtained by Dumas and Laurent from coal-tar. Using the information which had been already obtained in the research on quinone, Graebe and Liebermann now assumed that alizarin must be a dihydroxyquinone of anthracene, the relation of these substances to one another being easily seen from the following formulæ:—

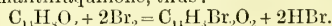


Having thus obtained anthracene from alizarin it was now only necessary to reverse the operation and convert anthracene into alizarin, and the problem of the artificial production of a vegetable colouring matter would be solved for the first time.

In 1862 Dr. Anderson, while investigating anthracene, obtained from it by oxidation a substance of the formula  $C_{11}H_8O_2$  which he named oxanthracene.

In this substance Graebe and Liebermann recognised the quinone of anthracene (anthraquinone), the first step in the synthesis of alizarin from anthracene, and in order to convert this quinone into alizarin all that was necessary was to replace two atoms of hydrogen in it by hydroxyl, an operation which is easily done in the following way:—

Anthraquinone when heated with two molecules of bromine in sealed tubes is converted into dibromanthraquinone, thus:



This substance when heated with potash exchanges each of its bromine atoms for (OK), yielding the potash salt of alizarin,  $C_{11}H_7(OK)_2O_2$ , a reaction which is precisely similar to the formation of chloranilate of potash from chloranil as described above. The potassic alizarate thus obtained, when decomposed with hydrochloric acid, yielded alizarin, and thus the problem of the artificial production of alizarin was solved.

In considering this synthesis, perhaps the most remarkable fact, from a chemical point of view, is that, in consideration of the number of possible isomers of alizarin, just that dibromanthraquinone prepared by Graebe and Liebermann should on treatment with potash have yielded alizarin. Had this not been so, the artificial production of alizarin would no doubt have been very much delayed.

The great importance of alizarin as a dyeing agent induced Graebe and Liebermann to patent this process, which proved, however, to be of no commercial value, owing to the great expense

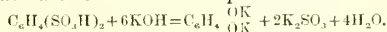


attending the use of bromine, and it was therefore desirable to find some new method which would render their discovery important from a manufacturing point of view.

This was first achieved by W. H. Perkin<sup>1</sup> in the following way:—Sulphuric acid, as is well known, forms with many organic bodies compounds called sulphonic acids, which in composition simply correspond to the substance acted on plus sulphuric anhydride.

Thus benzene  $C_6H_6$ , when treated with sulphuric acid yields benzenesulphonic acid  $C_6H_5SO_3H$ . Naphthalene  $C_{10}H_8$ , naphthalenesulphonic acid  $C_{10}H_7SO_3H$ . When fused with caustic potash these sulphonic acids are split up into the potassium salt of the corresponding phenol and potassium sulphite thus:—

$C_6H_5SO_3H + 3KOH = C_6H_5OK + K_2SO_3 + 2H_2O$ .  
Similarly disulphonic acids when fused with potash are converted into diphenols thus:—



In this second example it will be seen that a body is formed which bears the same relation to benzene as alizarin does to anthraquinone, and it was therefore probable that if anthraquinone were subjected to a similar series of reactions, alizarin would result.

The great obstacle to carrying out this synthesis, in the first instance, was the remarkable stability of anthraquinone in general and particularly towards sulphuric acid, which is so great that it dissolves in moderately hot sulphuric acid without change, and crystallises out again in needles on cooling.

When, however, a mixture of anthraquinone and sulphuric acid was heated very strongly, combination did eventually take place, the product becoming perfectly soluble in water, the solution now containing mono- and disulphonic acids of anthraquinone.

After removing the excess of sulphuric acid from the new product it was mixed with caustic potash, and heated to about  $180^\circ C$ .

During the heating the melt became darker and darker in colour, and eventually almost black, and on dissolving this in water a rich purple solution was obtained which when acidified with dilute sulphuric acid gave a copious precipitate of alizarin.

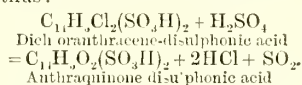
The great obstacle to the preparation of alizarin—viz. the use of bromine—was thus removed, and, as the future has proved, a process had been obtained by which this colouring matter could be manufactured in quantity and at a price so cheap as entirely to supersede the old method of dyeing with the madder root.

Another process for the manufacture of artificial alizarin shortly afterwards discovered by W. H. Perkin, and largely used by him on a manufacturing scale, is the following:—

Anthracene is treated with chlorine and thus converted into a beautifully crystalline compound called dichloranthracene  $C_{14}H_8Cl_2$ .

This substance combines with Nordhausen sulphuric acid, forming a bright-green solution, which contains a sulphonic acid of dichloranthracene. When heated with sulphuric acid

this substance undergoes a remarkable change, hydrochloric acid and sulphurous acid are evolved, and a disulphonic acid of anthraquinone formed thus:—



This anthraquinone disulphonic acid when fused with potash yields alizarin.

Alizarin and the other colouring matters of this class will not dye unprepared fabrics; these must first of all be mordanted.

The mordants used in this case consist of metallic hydroxides—e.g. of aluminium, iron, and chromium. Chloride of tin (tin crystals) is also extensively employed.

With alumina mordants alizarin produces shades of red and pink; with iron mordants, shades of black and purple; with chromium mordants, a dull purple; and with tin crystals a bright yellowish orange. These mordants may also be mixed and thus a large variety of different shades produced. A description of the method of application of these various mordants and the processes employed in dyeing with alizarin will be found in the article DYEING.

Since the first production of artificial alizarin on the large scale, the study of this substance and of the various colouring matters related to it has received a large amount of attention at the hands of chemists, the result being that a considerable number of derivatives of anthraquinone have been prepared and examined.

Most of these are either colouring matters themselves, or easily converted into such, several of them being obtained on the large scale in the manufacture of alizarin.

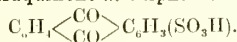
These derivatives may be divided under the following heads:—

- (1) Sulphonic acids of anthraquinone.
- (2) Monohydroxyanthraquinones.
- (3) Dihydroxyanthraquinones.
- (4) Trihydroxyanthraquinones.

In this article are also included the two dyeing matters, Gallein and Cærolein, which although not actually anthracene derivatives are very closely allied to these.

### Sulphonic acids of anthraquinone.

#### 1. Anthraquinone-*m*-sulphonic acid



This acid is formed together with a certain amount of anthraquinone disulphonic acid by heating anthraquinone with fuming sulphuric acid to  $170^\circ$  or with ordinary sulphuric acid to  $250^\circ-260^\circ$ .

In preparing it a mixture of one part of fuming sulphuric acid (containing 40.50 p.c. anhydride) and 1-1½ parts of anthraquinone is gradually heated to about  $170^\circ$  and kept at this temperature for eight or ten hours, the whole being well stirred during the operation.

The product thus formed consists chiefly of the mono-sulphonic acid together with a little disulphonic acid and unchanged anthraquinone. On diluting with water the anthraquinone separates out, and can easily be filtered off, leaving the sulphonic acids in solution. In order to sepa-

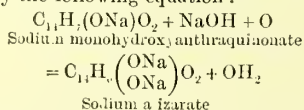
<sup>1</sup> It should be mentioned here that while these experiments were in progress, Caro, Graebe and Liebermann were investigating the same reaction in Germany.

rate the mono- from the disulphonic acid the clear filtrate is neutralised with carbonate of soda (or caustic soda). This causes the difficultly soluble sodium salt of anthraquinone monosulphonic acid to separate out, leaving the easily soluble salt of the disulphonic acid in solution.

The pasty mass obtained on neutralising with soda is thoroughly pressed, washed with a little water, and then if required pure recrystallised from this solvent. In this way a beautiful brilliant-white sealy crystalline mass is obtained, which consists of pure sodic anthraquinone monosulphonate, the so-called 'silver salt' of the alizarin manufacturer.

The free acid obtained by the addition of an acid to the soda salt crystallises in plates. It is very easily soluble in cold water and alcohol, but almost insoluble in ether.

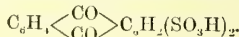
When fused with caustic soda, this acid (or rather its soda salt) gives first hydroxyanthraquinone  $C_6H_2<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>C_6H_4OH$ , and then alizarin; and, as will be shown later on, alizarin, when prepared on a manufacturing scale, is invariably formed from the monosulphonic acid of anthraquinone, not from the disulphonic acid as might be expected. The reason for this is that on fusing hydroxyanthraquinone with caustic soda, a continuous process of oxidation and reduction is carried on, the change being represented by the following equation:—



the oxygen being supplied at the expense of a part of the hydroxyanthraquinone which is thereby reduced to anthraquinone. On the large scale this reduction is prevented by the use of chlorate of potash in the fusion.

*Literature.*—Graebe and Liebermann (A. 160, 131; 212, 44; B. 7, 805).

#### Anthraquinone disulphonic acids



When anthraquinone is heated to a high temperature with 2 or 3 parts of ordinary or better fuming sulphuric acid, a mixture of  $\alpha$ - and  $\beta$ -anthraquinone disulphonic acid is obtained, which can be separated by fractional crystallisation of the sodium salts.

*Preparation.*—1. A mixture of 10 kilos of anthraquinone and 20 to 30 kilos of fuming sulphuric acid is heated to a temperature of 160°–170° until a sample taken out is found to dis-

solve completely in water. The product is then heated another hour to convert any mono- into disulphonic acid, poured into water, neutralised with caustic soda, and evaporated.—2. 10 kilos of anthraquinone, 12 kilos of hydrogen sodium sulphate, and 40 kilos of ordinary concentrated sulphuric acid are heated in pressure tubes for five or six hours to 260°, the product treated with water, and the acids converted into sodium salts as above.

In concentrating the solution of the sodium salt obtained by either of the above methods, the sodium salt of the  $\alpha$ -acid crystallises out first, the more readily soluble salt of the  $\beta$ -acid remaining in the mother-liquors, and thus by repeated recrystallisation, the two acids are easily separated from one another.

The free acids obtained by decomposing the salts by an acid are both readily soluble in alcohol and water, but insoluble in ether and benzene, the  $\alpha$ -acid crystallises in small yellow crystals, the  $\beta$ -acid in beautiful yellow plates.

The salts of the  $\alpha$ -acid are sparingly soluble in water and crystallise with difficulty, those of the  $\beta$ -acid are readily soluble and crystallise with the greatest ease.

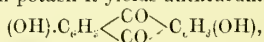
Besides these two important acids, two further disulphonic acids of anthraquinone are known—viz.,  $\chi$ -anthraquinone disulphonic acid and  $\rho$ -anthraquinone disulphonic acid.

*Literature.*—Schultz (Chemie des Steinkohlentheers, 709, 712); Perkin (C. J. 1870, 133); Graebe and Liebermann (A. 160, 134).

**$\chi$ -Anthraquinone disulphonic acid.** This acid is formed by treating sodium  $\alpha$ -anthracene disulphonate with nitric acid. The sodium salt crystallises in yellow prisms, which are sparingly soluble in water. On fusing with potash this salt yields chrysazin  $C_{12}H_8(OH)_2O_2$ , hydroxychrysazin  $C_{12}H_8(OH)_2O_2$ , *m*-hydroxybenzoic acid, and salicylic acid.

*Literature.*—Liebermann and Dehnst (B. 12, 1288).

**$\rho$ -Anthraquinone disulphonic acid** is obtained by oxidising  $\beta$ -anthracene disulphonic acid. The soda salt crystallises in leather-yellow plates, which are easily soluble in water. On fusing with potash it yields anthraflavin

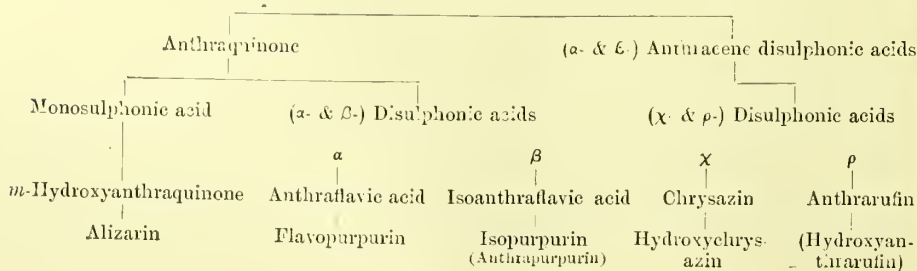


hydroxychrysazin  $C_{12}H_8(OH)_2O_2$ , *m*- and *o*-hydroxybenzoic acids.

*Literature.*—Liebermann and Dehnst (*loc.*).

The relation of the various colouring matters of this group to anthracene, anthraquinone, and its sulphonic acids is easily understood from the following table (Schultz):—

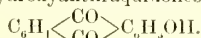
#### Anthracene



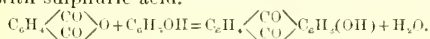
The behaviour of the anthraquinone disulphonic acids on fusion with potash is exactly similar to that of the monosulphonic acid. Just as this acid on fusion with potash is first converted into monohydroxyanthraquinone and then by oxidation into dihydroxyanthraquinone (alizarin), so the anthraquinone disulphonic acids in the first place yield the corresponding dihydroxyanthraquinones, which then by the further action of the potash are converted into trihydroxyanthraquinones.

### Hydroxyanthraquinones.

#### I. Monohydroxyanthraquinones



*o*-Hydroxyanthraquinone (*Erythroxyanthraquinone*). This substance is formed together with *m*-hydroxyanthraquinone by strongly heating a mixture of phenol and phthalic anhydride with sulphuric acid.



Also by heating *o*-bromanthraquinone with potash to 160°.

*o*-Hydroxyanthraquinone crystallises from alcohol in orange-red needles, which melt at 190°. When fused with potash it gives alizarin.

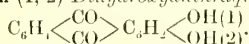
*Literature*.—Baeyer and Caro (B. 7, 969); Peckmann (B. 12, 2128).

*m*-Hydroxyanthraquinone is easily prepared by melting anthraquinone sulphonic acid or *m*-bromanthraquinone with potash. Synthetically it has been prepared (together with *o*-hydroxyanthraquinone) by heating together phthalic anhydride, phenol and sulphuric acid (*v. supra*). It crystallises from alcohol in yellow plates, which melt at 323°, and sublimes readily at a higher temperature. When fused with potash it is converted into alizarin. A mixture of *o*- and *m*-hydroxyanthraquinone can easily be resolved into its constituents by means of baryta water, with which *o*-hydroxyanthraquinone forms an insoluble compound, whereas the barium salt of *m*-hydroxyanthraquinone is readily soluble.

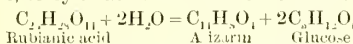
*Literature*.—Graebe and Liebermann (A. 160, 111); Baeyer and Caro (B. 7, 969).

#### Dihydroxyanthraquinones.

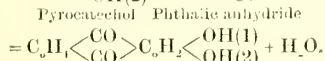
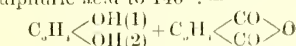
##### Alizarin (1, 2) Dihydroxyanthraquinone



Alizarin occurs in madder (the root of *Rubia tinctoria*) as rubianic acid, and is obtained from this glucoside either by the action of a ferment, or by treatment with a dilute acid:—



Alizarin is prepared artificially by fusing dichloranthraquinone, dibromanthraquinone, anthraquinone, mono- or disulphonic acids with potash. It is produced synthetically when a mixture of pyrocatechol and phthalic anhydride is heated with sulphuric acid to 110°:—



Alizarin

**Purification of artificial alizarin.** Commercial alizarin contains as impurities hydroxy-

anthraquinone, anthrapurpurin, flavopurpurin, and small quantities of other colouring matters.

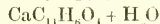
In order to separate the alizarin from these, the crude commercial product is dissolved in dilute caustic soda, and the solution treated with carbonic acid until two-thirds of the colouring matter has been precipitated as acid sodium salt. The precipitate is collected, washed with water, decomposed with hydrochloric acid, the crude alizarin thus obtained dissolved in caustic soda, and the treatment with carbonic acid repeated twice more.

The purified product is then boiled with baryta water to remove hydroxyanthraquinone and anthraflavie acid (which dissolve), the barium salt of alizarin is collected, washed, decomposed by hydrochloric acid, and the alizarin either sublimed or recrystallised from alcohol.

**Alizarin** crystallises from alcohol in red needles or prisms, which melt at 282°, and sublime at a higher temperature. With care alizarin can be sublimed in magnificent deep-red prisms, which, if the operation be performed on a large scale, may be obtained over an inch in length.

It dissolves in alkalis with a purple colour, and is completely precipitated from this solution by the addition of lime or baryta in the form of a blue precipitate of the calcium or barium salt. Heated with acetic anhydride to 160° alizarin forms a diaetyl compound  $C_{12}H_8O_2(C_2H_3O)_2$ , which crystallises from alcohol in long yellow needles, melting at 160°. When treated with nitrous acid alizarin yields anthraquinone. Nitric acid acts violently on alizarin with evolution of red vapours and formation of phthalic and oxalic acids. Distillation with zinc reduces alizarin to anthraene.

#### Salts of alizarin. Calcium alizarate



is precipitated by adding calcium chloride to an ammoniacal solution of alizarin as a purple mass. *Barium alizarate*  $BaC_{12}H_8O_8 + H_2O$  is prepared, like the calcium salt, by mixing an alkaline solution of alizarin with barium chloride. It is deep-violet when moist, almost black when dry, and very sparingly soluble in water. *Aluminium alizarate*  $(C_{12}H_8O_8)_2Al_2O_3(?)$  is obtained by precipitating an alkaline solution of alizarin with alum or aluminium hydroxide. It is a very fine red, or rose-red precipitate. *Lead alizarate*  $C_{12}H_8O_8Pb$  is obtained by mixing an alcoholic solution of alizarin with an alcoholic solution of sugar of lead.

Alizarin can readily be detected by means of the spectroscope, as it gives in alkaline solution two sharp absorption bands, one at *d* and one near *c*, as will readily be seen from the accompanying figure, which shows the absorption spectrum of a solution of alizarin in alcoholic potash.



*Literature*.—Anderson (J. 1817-18, 749); Stenhouse (J. 1864, 543); Roehleder (B. 3, 295); Perkin (C. J. 23, 111); Graebe and Liebermann (A. Suppl. 7, 309; B. 3, 359); Baeyer and Caro (B. 7, 972); Liebermann (A. 183, 206);



Liebermann and Dehnst (B. 12, 1293); Schunck (A. 66, 187); Wolff and Strecker (A. 75, 8).

**Derivatives of alizarin.** When treated with the ordinary re-agents, such as bromine, nitric acid, &c., alizarin forms a variety of valuable substitution products, some of which are used to a considerable extent as dyeing agents. The most important of these are the following:—

**Monobromalizarin**  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown \end{smallmatrix} C_6H_3Br(OH)_2$

This substance is prepared by heating alizarin with bromine and bisulphide of carbon to  $183^\circ$ – $190^\circ$  for four or five hours.

It crystallises from glacial acetic acid in orange-coloured needles which, when heated, first melt to an orange-coloured liquid and then sublime in orange-red needles.

As a dyeing agent, monobromalizarin retains all the properties of combining with mordants possessed by alizarin, and the colours produced appear to be equally fast. The shade of colour produced is, however, not the same, the reds being less purple, and the purples less blue than those produced by alizarin.

**Literature.**—Perkin (C.J. 27, 401)

**$\alpha$ -Nitroalizarin**  $C_6H_4(NO_2)O_2$ . This substance is obtained by treating diacetyl alizarin with nitric acid.

**Preparation.**—Diacetylalizarin in fine powder is gradually added to nitric acid (sp.gr. 1.5) cooled with ice. The resulting dark-red-coloured liquid is poured into an excess of water, and the yellow precipitate, thus formed, is collected, well washed with cold water, and then boiled with water to dissolve out a small quantity of an orange-coloured secondary product. The residue is dissolved in hot dilute caustic potash, the resulting blue-violet solution acidified with hydrochloric acid, and the precipitate recrystallised from alcohol.  $\alpha$ -Nitroalizarin crystallises from alcohol or glacial acetic acid in golden yellow needles. It dissolves in caustic alkali with a blue-violet colour, but if only a minute quantity of alkali is employed the solution is of a fine crimson colour. The alkaline solution gives two absorption bands similar to alizarin. Nitroalizarin is easily reduced in alkaline solution with sodium amalgam, amidoalizarin  $C_6H_4(NH_2)O_2$  resulting.

**$\alpha$ -Amidoalizarin** crystallises from alcohol in small needles of a nearly black colour, but possessing a slight greenish metallic reflection. Its alcoholic solution gives two absorption bands; the first is a little beyond  $\mu$  and the second near  $\epsilon$ . There is also a faint line close to  $\epsilon$ .

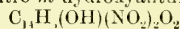
**Dyeing Properties of  $\alpha$ -Nitro- and  $\alpha$ -Amidoalizarin.** These colouring matters possess the power of dyeing ordinary madder mordants.  $\alpha$ -Nitroalizarin gives with alumina mordants very clear orange-red colours, not unlike some of the colours produced with aurine, and with iron mordants reddish-purple colours. Amidoalizarin gives with alumina mordants purple colours, and with iron a bluish or steel-like colour. The great beauty of the colours produced by  $\alpha$ -nitroalizarin makes it a most valuable dyeing agent. It is, however, not manufactured on the large scale, owing to the expense attendant on its preparation, and up till now no cheaper method has been found for producing it than the above.

**Literature.**—Perkin (C. J. 30, 578).

#### $\beta$ -Nitroalizarin

$C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown \end{smallmatrix} C_6H_3(NO_2)(OH)_2(OH:OH:NO_2 = 1:2:3)$

$\beta$ -Nitroalizarin is prepared by the action of nitrous fumes or nitric acid on alizarin, and also by boiling dinitro-*m*-hydroxyanthraquinone



with caustic soda (20 p.c.).

**Preparation.**—1 part of alizarin suspended in 10 parts of glacial acetic acid is carefully mixed with 0.7 parts of nitric acid (of  $42^\circ B.$ ).

The mixture is allowed to stand at the ordinary temperature until the precipitate, on examination with the spectroscope, is found to contain no more alizarin. The whole is then filtered, the residue dissolved in warm dilute potash solution, reprecipitated with hydrochloric acid, and the crude nitroalizarin purified by recrystallisation from glacial acetic acid.  $\beta$ -Nitroalizarin crystallises in orange-yellow needles which melt with decomposition at  $244^\circ$ . When carefully heated it sublimes, with a good deal of decomposition, in yellow needles. Dissolved in alkalis it forms a purple solution; the sodium salt is insoluble in an excess of caustic soda. The calcium salt is an insoluble violet-red precipitate, which is not decomposed by carbonic acid (distinction from alizarin). Treated with glycerin and sulphuric acid,  $\beta$ -nitroalizarin is converted into alizarin blue.

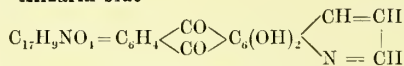
The diacetate of  $\beta$ -nitroalizarin crystallises in yellow needles melting at  $218^\circ$ .

$\beta$ -Nitroalizarin is prepared on the large scale, and comes into the market under the name of 'Alizarin orange.' In dyeing it is applied to the various fibres in the same way as alizarin; but although it yields fast colours, it has as yet found only comparatively limited employment. Applied to wool it gives the following shades:—

With an aluminium mordant it yields a very good orange; with stannous chloride mordant a reddish or yellowish orange according to the amount of mordant used; with copper sulphate mordant a good reddish-brown is obtained; with ferrous sulphate a purplish-brown; and with bichromate of potash a dull brownish-red.

**Literature.**—Rosenstiehl (Bl. 26, 63); Schunck and Roemer (B. 12, 584); Simon (B. 15, 692).

#### Alizarin blue



(OH:OH:N:CH = 1:2:3:4).

This important colouring matter, discovered by Prud'homme, is obtained by treating  $\beta$ -nitroalizarin with glycerin and sulphuric acid. Its chemical constitution was first demonstrated by Graebe, who showed that this substance was related to alizarin in precisely the same way as quinoline is to benzene, *i.e.* that alizarin blue is a quinoline of alizarin.

**Preparation.**—1 part of  $\beta$ -nitroalizarin, 5 parts sulphuric acid, and  $1\frac{1}{2}$  glycerin (of sp.gr. 1.262) are mixed and gently heated.

At  $107^\circ$  the reaction commences and soon becomes very violent, the temperature rising to  $200^\circ$ . After the frothing has subsided, the mass is poured into water, the product well boiled,

filtered, and the residue extracted three or four times with very dilute sulphuric acid. The combined extracts on cooling deposit the crude alizarin blue sulphate in brown crystals. These are collected, washed with water till neutral, mixed with water, and borax added until the solution becomes brownish-violet. The precipitate thus formed is filtered off, washed with water, and decomposed with a dilute acid, the crude alizarin blue thus obtained being purified by recrystallisation from benzene or glacial acetic acid.

Alizarin blue crystallises from benzene in brownish-violet needles which melt at  $270^{\circ}$ , and at a higher temperature gives off orange-red vapours which condense in the form of blue needles.

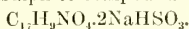
It is insoluble in water, sparingly soluble in alcohol and ether, more readily soluble in hot benzene. It dissolves in ammonia, potash or soda, forming blue solutions which become green when mixed with an excess of alkali.

Alizarin blue combines with both bases and acids.

The barium salt  $\text{BaC}_{12}\text{H}_8\text{NO}_4\text{BaO} + \frac{1}{2}\text{H}_2\text{O}$  is a greenish-blue precipitate. The following salts of alizarin blue with acids have been prepared:—

$\text{C}_{12}\text{H}_8\text{NO}_4\text{HCl}$  is a red crystalline precipitate formed by passing dry hydrochloric acid gas through a solution of alizarin blue in boiling benzene. When treated with water it is completely decomposed into its constituents. The sulphate crystallises in red needles. The acetate  $\text{C}_{12}\text{H}_8\text{NO}_4\text{C}_2\text{H}_3\text{O}_2$  crystallises in blue plates.

Alizarin blue also combines with picric acid forming a compound  $\text{C}_{12}\text{H}_8\text{NO}_4\text{C}_6\text{H}_3(\text{NO}_2)_3\text{O}$  which crystallises from benzene in long orange-red prisms melting at  $245^{\circ}$ . This compound is completely decomposed by water. One of the most important compounds of alizarin blue is the sodium bisulphite compound



This product is manufactured on the large scale and sold under the name of 'Alizarin Blue S.' It dissolves readily in water, with a brownish-red colour. Alizarin blue is met with in commerce in two forms, viz. as a paste containing about 10 p.e. of dry substance, and as a powder under the name of Alizarin Blue S. The former is nearly insoluble in water, while the latter, which is the bisulphite compound (described above), dissolves readily. This soluble kind is now almost entirely used in dyeing. In dyeing cotton with alizarin blue a chromium mordant is used, but in the case of wool, bichromate of potash gives the best results.

Alizarin blue with an alumina or iron mordant is also used for dyeing silk.

Alizarin blue is used largely as a substitute for indigo in calico-printing works. It is one of the most stable colouring matters, and is even said to be faster than indigo itself.

*Literature.*—Prud'homme (Bl. 28, 62); Graebe (A. 201, 333); Auerbach (C. J. 35, 800).

(1, 3) **Dihydroxyanthraquinone Purpuroxanthin**

$$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}_6\text{H}_2 \begin{array}{c} \diagup \text{OH}(1) \\ \diagdown \text{OH}(3) \end{array}$$

Purpuroxanthin exists in small quantities in madder. It can be prepared by heating purpurin

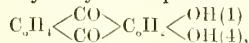
$\text{C}_{14}\text{H}_8(\text{OH})_2\text{O}_2$  with iodide of phosphorus and water, or more readily by boiling purpurin with caustic soda and chloride of tin.

*Preparation.*—Purpurin is dissolved in a boiling solution of caustic soda (10 p.e.), and chloride of tin added until the solution loses its deep-red tint and becomes of a yellow colour. Hydrochloric acid is then added, the precipitate washed with strong hydrochloric acid, dissolved in baryta water, reprecipitated with hydrochloric acid and crystallised from alcohol.

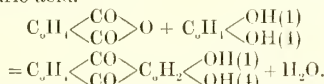
Purpuroxanthin crystallises in reddish-yellow needles which melt at  $262^{\circ}$ – $263^{\circ}$ . It dissolves in alkalis with a reddish colour. If the solution in caustic potash be boiled in the air, it absorbs oxygen, the purpuroxanthin being reconverted into purpurin.

*Literature.*—Schützenberger and Schiffré (Bl. 1, 12).

(1, 4) **Dihydroxyanthraquinone Quinizarin**



is obtained by heating a mixture of quinol (or *p*-chlorphenol) and phthalic anhydride with sulphuric acid.



*Preparation.*—Equal parts of *p*-chlorphenol and phthalic anhydride are heated to  $200^{\circ}$ – $210^{\circ}$  for some hours, with ten times as much sulphuric acid as chlorphenol used. The product is poured into two or three times its volume of water, and after standing for twenty-four hours, the precipitate is filtered off, washed and pressed.

The crude product is then boiled with water to free it from phthalic acid, dissolved in caustic soda, precipitated with hydrochloric acid and recrystallised from alcohol. In order to remove a small quantity of purpurin, which is nearly always present, the crude quinizarin is then washed with cold dilute caustic soda as long as the solution is coloured red, and the residue recrystallised from toluene.

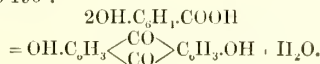
Quinizarin crystallises from alcohol in red needles which melt at  $192^{\circ}$ – $193^{\circ}$ , and sublime at a high temperature with partial decomposition. It dissolves readily in benzene. The solutions in ether and sulphuric acid are characterised by a beautiful greenish-yellow fluorescence. Quinizarin dissolves in baryta, forming a blue solution from which it is reprecipitated on passing carbonic acid (distinction from alizarin).

When fused with potash it is converted into hydroxychrysazin  $\text{C}_{14}\text{H}_8\text{O}_4$ . Quinizarin forms a diacetate which melts at  $200^{\circ}$ .

*Literature.*—Bayer and Caro (B. 8, 152); Sehneek and Roemer (B. 10, 554).

**Anthraflavic acid**  $\text{OHC}_6\text{H}_3 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{C}_6\text{H}_3\text{OH}$ .

Anthraflavic acid is prepared by fusing  $\alpha$ -anthraquinone disulphonic acid with potash, and is therefore nearly always present in artificial alizarin. Synthetically it has been obtained by heating *m*-hydroxybenzoic acid with sulphuric acid to  $190^{\circ}$ .



This mode of formation proves that this substance contains the two hydroxyl groups in different benzene rings.

**Anthraflavic acid** crystallises from alcohol in yellow needles which melt above  $330^{\circ}$ . The pure substance when carefully heated sublimes partially in yellow needles, leaving a considerable quantity of a carbonaceous residue. Anthraflavic acid does not dye mordanted cloth. It dissolves in alkalis forming a yellowish-red solution, and in sulphuric acid forming a green solution, the absorption spectrum of which shows a broad band between the blue and the green. Anthraflavic acid forms a number of salts of which the sodium salt is the most characteristic. This salt is sparingly soluble in water, and is remarkable for the ease with which it crystallises; this distinguishes it from isoanthraflavic acid, and gives a ready means of separating these two substances. When treated with acetic anhydride, anthraflavic acid forms a diacetate melting at  $228^{\circ}$ - $229^{\circ}$ .

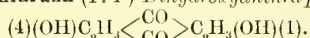
*Literature.*—Perkin (C. J. 1871, 24, 1109; 26, 19); Schunck and Roemer (B. 9, 379; 11, 970); Liebermann (B. 5, 963); Rosenstiehl (Bl. 29, 401-434); Barth and Senhofer (B. 170, 100).

**Isoanthraflavic acid**  $C_{11}H_5O_4$  is formed when  $\beta$ -anthraquinone disulphonic acid is fused with potash, and is therefore always contained in crude alizarin. In preparing it, crude alizarin is dissolved in dilute caustic soda, the solution precipitated with hydrochloric acid, and the precipitate dissolved in cold baryta water and filtered. (In this way isoanthraflavic acid, which forms a soluble baryta compound, is easily separated from alizarin, anthrapurpurin, and anthraflavic acid, which yield insoluble barium compounds.) The filtrate is treated with hydrochloric acid and the precipitate recrystallised from alcohol. Anthraflavic acid crystallises in long yellow needles, containing 1 mol.  $H_2O$ , which can be driven off at  $150^{\circ}$ . It melts above  $330^{\circ}$  and sublimes at a high temperature in lustrous yellow needles. It dissolves easily in alkalis forming a deep-red solution, but it does not dye mordanted cloth. Fused with potash isoanthraflavic acid yields anthrapurpurin.

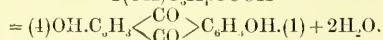
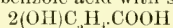
The diacetate of isoanthraflavic acid melts at  $195^{\circ}$ .

*Literature.*—Schunck and Roemer (B. 9, 379).

**Anthrarufin** (1:4') *Dihydroxyanthraquinone*



Anthrarufin is formed together with anthraflavic acid and metabenzdioxanthraquinone by heating *m*-oxybenzoic acid with sulphuric acid.



It may also be obtained by fusing *o*-anthraquinonedisulphonic acid with potash. Anthrarufin crystallises in yellow needles which melt at  $230^{\circ}$ , and sublime easily at a higher temperature (distinction from anthraflavic acid). It dissolves with difficulty in ammonia and soda, but more readily in potash.

Anthrarufin dissolves in sulphuric acid, forming a deep-red solution, the colour of which is so intense that it is still easily apparent in solutions containing only 1 part in 10,000,000.

Anthrarufin forms a diacetate which melts at  $244^{\circ}$ - $245^{\circ}$ .

*Literature.*—Schunck and Roemer (B. 11, 1173); Liebermann and Dehnst (B. 12, 1239).

**Metabenzdihydroxyanthraquinone**  $C_{11}H_6O_4$  is formed together with anthraflavic acid and anthrarufin by heating *m*-hydroxybenzoic acid with sulphuric acid (*v. supra*). It is separated from these by treatment with benzene and subsequent recrystallisation from dilute alcohol. Metabenzdihydroxyanthraquinone forms yellowish needles which melt at  $231^{\circ}$ - $293^{\circ}$ , and sublime at a higher temperature almost without decomposition. It dissolves in alkalis with a dark-yellow colour, and in concentrated sulphuric acid, forming a brownish-yellow solution, which shows no absorption bands.

The diacetate of metabenzdihydroxyanthraquinone melts at  $199^{\circ}$ .

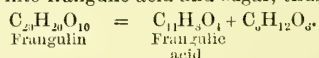
*Literature.*—Schunck and Roemer (B. 10, 1225); Rosenstiehl (B. 9, 946).

(1, 1' or 3, 3') **Dihydroxyanthraquinone** (*Chrysazin*) is formed by fusing  $\chi$ -anthraquinonedisulphonic acid with potash, or by treating hydrochrysamid  $C_{11}H_7(NH_2)(OH)_2O_2$  with nitrous acid and alcohol. (N.B. Hydrochrysamid is obtained by the reduction of chrysammic acid  $C_{11}H_7(NO_2)_2O_4$ , which is the product of the action of nitric acid on aloes.)

Chrysazin forms reddish-brown needles which melt at  $191^{\circ}$ . It dissolves in alkalis and sulphuric acid, with a red colour. Its diacetate melts at  $227^{\circ}$ - $232^{\circ}$ .

*Literature.*—Liebermann (A. 183, 184).

**Frangulic acid**  $C_{11}H_8O_4$ . The glucoside frangulin when boiled with dilute acids is converted into frangulic acid and sugar, thus:—

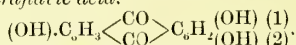


It crystallises from alcohol in yellowish-red needles, which melt at  $252^{\circ}$ - $254^{\circ}$ , and sublime readily on further heating with slight decomposition. It dissolves in alkalis forming a cherry-red solution. Its diacetate melts at  $184^{\circ}$ .

*Literature.*—Faust (A. 165, 231).

### **Trihydroxyanthraquinones.**

**Anthrapurpurin.** *Isoapurpurin.* *Hydroxy-isoanthraflavic acid.*



This important colouring matter is contained in crude artificial alizarin. It is formed by fusing  $\beta$ -anthraquinonedisulphonic acid, isoanthraflavic acid, metabenzdihydroxyanthraquinone, or  $\alpha$ -dibromanthraquinone with potash.

The preparation of this substance is a somewhat tedious process dependent on the fact that anthrapurpurin differs from alizarin, in the behaviour of its alumina lake. The former, on treatment with an alkaline carbonate, is dissolved, whilst the alizarin lake remains unattacked. The solution containing the anthrapurpurin is filtered from the alizarin lake, heated to boiling, and acidified with hydrochloric acid. The anthrapurpurin thus obtained is purified by conversion into its difficultly soluble sodium compound, and from this, by precipitation with barium chloride, the barium salt is obtained which is decomposed with hydrochloric acid. The precipitate is collected on a filter, well washed with water and recrystallised from glacial acetic acid.



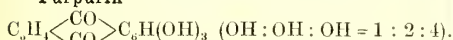
Anthrapurpurin crystallises in orange-coloured needles which melt above 330°, and, when carefully heated, sublime in long red needles. It dissolves in alkalis with a violet colour; the solution shows the same absorption spectrum as alizarin.

With acetic anhydride anthrapurpurin forms a triacetate  $C_{11}H_3(C_2H_3O_2)_3O_6$ , which crystallises in yellow needles, melting at  $220^\circ$ . When heated with ammonia, anthrapurpurin is converted into anthrapurpurinamide  $C_{11}H_4(NH_2)(OH).O_6$ .

Anthrapurpurin has the same affinity for mordants as alizarin; the colours it produces are also analogous to some extent, as it produces reds with alumina, purples and blacks with iron mordants. There is, however, a considerable difference in the shade of colour produced, the reds being much purer and less blue than those of alizarin, whilst the purples are bluer and the blacks more intense. When used in Turkey-red dyeing it produces very brilliant colours of a scarlet shade, which are of remarkable permanence.

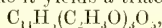
*Literature.*—Perkin, 25, 659; 26, 425; 29, 851; Caro (B. 9, 682); Schunck and Roemer (B. 9, 679; 10, 972, 1823; 13, 42); Rosenstichl (Bl. 29, 405); Auerbach (J. 1874, 488).

## Purpurin



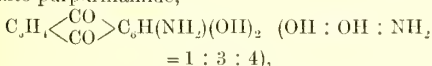
Purpurin occurs along with alizarin in madder, probably as glucoside. In order to separate it from alizarin, the mixture of the two substances is repeatedly recrystallised from a hot solution of alum, in which purpurin is more soluble than alizarin, or the mixture is dissolved in caustic soda and the solution saturated with carbonic acid. This precipitates the alizarin, but not the purpurin.

Purpurin crystallises from dilute alcohol in long orange-coloured needles which contain 1 mol.  $\text{H}_2\text{O}$ . The pure substance begins to sublime at  $150^\circ$ , and melts at  $253^\circ$ . It is slightly soluble in water, forming a deep yellow solution; in alkalis it dissolves with a purple-red colour; in alkaline carbonates with a red colour. The solution in alkalis shows two marked absorption bands in the green. Purpurin also dissolves readily in ether, carbon bisulphide, benzene, and acetic acid; these solutions give two absorption bands, one at  $\epsilon$  and the other near  $\epsilon$ ; the solution in sulphuric acid shows another line in the yellow. Under the influence of reducing agents purpurin is converted into purpuroxanthin  $\text{C}_{11}\text{H}_8\text{O}_4$ ; when boiled with acetic anhydride it yields a triacetate.



which crystallises in yellow needles, melting at  $192^{\circ}$ - $193^{\circ}$ .

Aqueous ammonia at 150° converts purpurin into purpurinamide,

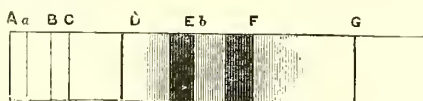


which, when boiled with ethyl nitrite, yields  
 purpuroxanthin,  $\text{C}_5\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_2\text{OH}$  (1)  
 purpuroxanthin,  $\text{C}_5\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_2\text{OH}$  (3).

Purpurin dyes fabrics much in the same way as alizarin and anthrapurpurin, there being, however, a difference in the shades. The reds produced by purpurin are much yellower, and

the browns (with chrome mordant) much more intense than are produced either by alizarin or anthrapurpurin.

The following figure shows the absorption spectrum of a solution of purpurin in aluminium sulphate:—



Flavopurpurin occurs in commercial artificial alizarin, but is with difficulty isolated from this product, owing to the fact that its chemical properties agree so closely with those of anthrapurpurin, which is also nearly always present in artificial alizarin, that it can only with difficulty be separated from this substance.

It is prepared by fusing  $\beta$ -anthraquinone-disulphonic acid or anthratlavic acid with potash.

Flavopurpurin crystallises from alcohol in anhydrous yellow needles, sparingly soluble in water, but readily soluble in cold alcohol. Its melting-point lies above 330°.

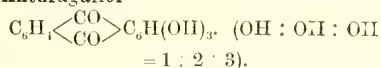
It dissolves in caustic alkalis with a purple colour; the solution shows two absorption bands, one in the blue and the other near the red, but a little further removed than the alizarin band.

Flavopurpurin dyes mordanted fabrics similarly to alizarin, there being, however, a slight difference in the shades produced. The red shade is somewhat duller and yellower; the brown shade is also yellower. Flavopurpurin dyes wool mordanted with tin crystals and cream of tartar a bright yellowish orange.

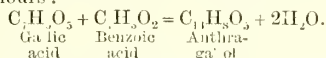
When heated with acetic anhydride, flavo-purpurin yields a triacetate  $C_{11}H_4(C_2H_3O)_3O_3$ , which crystallises from alcohol in golden-yellow plates melting at  $238^\circ$ .

*Literature.*—Caro (B. 9, 682); Schunck and Roemer (B. 9, 679; 10, 1823; 13, 42).

**Anthragallol**



Anthragallol is formed when a mixture of 1 part of gallic acid, 2 parts of benzoic acid, and 20 parts of sulphuric acid are heated to 125° for eight hours :



The product is poured into water, well washed, and recrystallised from alcohol.

Anthragallol crystallises in yellow needles, which, when heated to 290°, sublime without melting. It is sparingly soluble in water, chloroform, or carbon disulphide; readily soluble in alcohol, ether, and glacial acetic acid. It dissolves in alkalis, forming a green solution. Its triacetate,  $C_9H_5(C_2H_3O)_3$ , melts at  $171^{\circ}$ – $173^{\circ}$ .

*Literature.* Seuberlich (B. 10, 39).

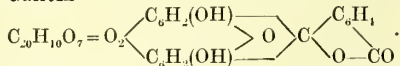
**Н. dioxanthanum** *Hydroxyanthracinum*

$C_{11}H_5O_5$ . Formed by fusing chrysazin, anthraquinone,  $\rho$ - or  $\chi$ -anthraquinonedisulphonic acids with potash. It crystallises in small red needles, which are sparingly soluble in alcohol. When strongly heated it sublimes in red needles. It

dissolves in potash, forming a violet solution, and shows in its reactions great similarity to purpurin. It differs from this substance in the fact that its solution in alum gives no absorption spectrum. The triacetate of hydroxyanthrarubin melts at  $192^{\circ}$ – $193^{\circ}$ .

*Literature.*—Liebermann (A. 183, 191); Schunck and Roemer (B. 11, 1179); Liebermann and Boeck (B. 11, 1617); Liebermann and Dehnst (B. 12, 1289).

#### Gallein



Gallein is formed by heating pyrogallol with phthalic anhydride.

*Preparation.*—A mixture of 1 part of phthalic anhydride and 2 parts of pyrogallol are heated to  $190^{\circ}$ – $200^{\circ}$ , the melt dissolved in alcohol, and the colouring matter precipitated by the addition of water. The crude gallein thus obtained is dissolved in alcohol, reprecipitated with water, and, after repeating this operation a few times, converted into the acetate by heating with acetic anhydride. This is recrystallised several times, and decomposed with potash.

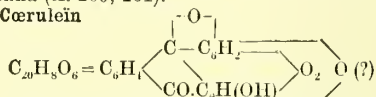
Gallein crystallises from alcohol in small greenish crystals. It is insoluble in chloroform and benzene, sparingly soluble in water and ether, readily soluble in alcohol, forming a dark-red solution. It dissolves in cold concentrated sulphuric acid without change; on warming the solution cœrulein is formed.

Gallein dissolves in small quantities of potash or soda with a red colour; excess of alkali produces a blue solution. Heated with acetic anhydride to  $150^{\circ}$  gallein yields a tetracetate of hydrogallein.

Gallein (often called anthracene violet) is sold in the form of a reddish-brown powder, or a 10 p.c. paste; not very soluble in cold water, but readily so in hot. With all the usual alizarin mordants gallein produces purple colours, which are fast to light and soap; those obtained by the use of chromium and iron are bluish, those with tin reddish, those with aluminium intermediate in tone.

*Literature.*—Baeyer (B. 4, 457 and 663); Buchka (A. 209, 261).

#### Cœrulein



Cœrulein is prepared by heating 1 part of gallein and 20 parts of sulphuric acid to  $200^{\circ}$ , and precipitating the colouring matter by adding a large quantity of water. It is thus obtained as a bluish-black mass, which, when rubbed, acquires a metallic appearance. It is almost insoluble in water, ether, and alcohol, more readily soluble in acetic acid.

It dissolves in alkalis with a green colour, in acids with an olive-brown colour. With bisulphite of soda cœrulein forms an easily soluble compound. With acetic anhydride it forms a triacetate. Cœrulein (anthracene green) is sold in two forms, either as a bluish-black paste containing 10–20 p.c. cœrulein, or as a black powder.

The former is insoluble in water, the latter, known as cœrulein S, is soluble in water,

and is indeed a bisulphite compound of cœrulein.

Cœrulein is mostly employed in calico-printing for producing very fast olive-green shades. Whatever the mordant used, only different shades of olive-green are produced.

*Literature.*—Baeyer (B. 4, 556, 663).

#### MANUFACTURE OF ALIZARIN.

1. *Anthraquinone process.*—Anthracene, the basis of alizarin, is obtained entirely from the coal-tar oils boiling above  $300^{\circ}$ , the so-called 'last runnings' of the tar distiller. These heavy oils are redistilled and the anthracene oils collected as soon as the distillate on cooling commences to solidify. In this way a semi-solid greenish-looking mass is obtained, which, after roughly freeing from excess of oil by treatment in hydraulic presses, is the starting point in the alizarin factory. This crude product contains only about 30–40 p.c. anthracene, the remainder consisting of phenanthrene, naphthalene, carbazol, and small quantities of other hydrocarbons.

The first operation necessary in the manufacture of alizarin is that of purifying the crude anthracene obtained from the tar distillers, in order to obtain a product fit for the subsequent oxidation to anthraquinone.

This process of purification varies considerably in different countries, but the following method may be given as having been used with much success.

The crude anthracene is first ground between edge-runners, and then thoroughly agitated with boiling petroleum spirit in large iron vessels fitted with stirrers and heated with steam.

About 1,500 to 1,800 lbs. of crude anthracene and 300 gallons of petroleum spirit are used in one operation, the amount of the latter varying slightly according to the quality of the anthracene employed. After boiling for an hour or two, the product is allowed to cool, filtered through coarse canvas, and the anthracene on the filter washed with a little clean petroleum spirit. The pasty mass thus obtained is next treated with steam to remove the excess of petroleum spirit, and then sublimed. The sublimation process is best carried out by melting the anthracene in an iron pot, called the 'subliming pot,' and then blowing in superheated steam. This carries the anthracene vapour forward through a long pipe, where it meets a spray of water, which serves to condense both it and the steam. The anthracene is thus obtained in an extremely finely divided state, much more suitable for oxidation than when simply ground under edge-runners as it used to be. The next step consists in converting the anthracene into anthraquinone by oxidation with bichromate of potash (or soda) and sulphuric acid—an operation which is usually done in the following way:—The anthracene is placed in lead-lined tanks with about twice its weight of potassic bichromate (dissolved in water), the requisite amount of dilute sulphuric acid is slowly added, and the mass kept well boiled and agitated by a steam jet connected with a Körtling's injector.

The whole is then transferred to settling tanks, the crude yellowish-brown anthraquinone well washed by decantation until free from green

chrome liquors, well drained, and freed from water as completely as possible by placing it in canvas bags and exposing it to great pressure in a hydraulic press. The amount of oxidiser required to convert the crude anthracene into anthraquinone is of course regulated by the purity of the sample employed, pure anthracene requiring about 1.66 times its weight of potassium bichromate to convert it into anthraquinone.

Instead of potassium bichromate, the sodium salt is now very often used on account of its cheapness.

The anthraquinone thus obtained is still very impure, and must be carefully purified before it can be converted into sulphonic acid. In purifying anthraquinone two methods may be employed:

(1) The anthraquinone is sublimed, and then recrystallised from high boiling coal-tar naphtha.

(2) The anthraquinone is treated with concentrated sulphuric acid.

When the first process is employed, the anthraquinone is melted in iron pots and subjected to the action of super-heated steam. The steam carries the vapour of the anthraquinone with it, and on condensation a fine, almost impalpable, powder is obtained, which, when dried and recrystallised from high-boiling coal-tar naphtha, consists of nearly pure anthraquinone.

In this country this process has now been almost abandoned; method (2) having entirely taken its place.

The working of this method is based on the fact that crude anthraquinone when treated with sulphuric acid at 100° dissolves, but is not acted on. The impurities, however, become converted into sulphonic acids, which, being easily soluble, can be removed by treating the product with water, when nearly pure anthraquinone is left behind.

In carrying out this operation a mixture of 1 part of crude anthraquinone and 3 parts of sulphuric acid is placed in large circular lead-lined iron pots, and heated by steam for twenty-four hours, the whole being continuously agitated by a stirrer.

The blackish-looking product is then run into shallow tanks, and exposed to the action of damp air, or a gentle current of steam, until the acid has become diluted. In a short time anthraquinone separates out as a light-brown crystalline powder, which, after washing by decantation, pressing, and thoroughly drying, is found to contain about 95 p.c. of pure substance.

The anthraquinone is now in a condition suitable for conversion into the sulphonic acid.

This operation, which consists in heating anthraquinone with fuming sulphuric acid, is conducted in large iron pots capable of holding from 30 to 40 gallons. The amount of fuming sulphuric acid employed depends on the nature of the sulphonic acid required. In preparing the monosulphonic acid, 1 part of fuming acid (containing 40-50 p.c.  $\text{SO}_3$ ) and 1 to 1½ parts of anthraquinone are used.

The mixture is gradually heated by means of an oil-bath to 170°, or even to 190°, and kept at this temperature for eight or ten hours, the stirrer being kept constantly in motion.

The product, which contains, besides anthraquinemonosulphonic acid, a little disulphonic acid, and some unacted-on anthraquinone, is diluted with water, passed through a filter-press

to remove the anthraquinone, and neutralised with caustic soda.

In a short time the whole becomes quite thick owing to the separation of the sparingly soluble soda salt of anthraquinemonosulphonic acid, the easily soluble salts of the disulphonic acids remaining in solution.

The crystalline salt is collected in filter-presses, washed with a little very dilute sulphuric acid, and thus obtained practically pure in beautiful, brilliant, pearly scales.

In preparing the disulphonic acids of anthraquinone, the operation is similar to the above, the only difference being that more fuming sulphuric acid is used and the sulphonation conducted at a much higher temperature (about 260°).

The next operation consists in the conversion of the product just described, and called 'soda salt,' into colouring matter, a change which is accomplished by heating it strongly with caustic soda and a little potassium chlorate.

If the potassium chlorate is not added, a considerable loss is incurred owing to the reducing action of a large quantity of nascent hydrogen, always formed during the fusion, which converts the soda salt partially into anthraquinone and hydroanthraquinone. The fusion is conducted in large wrought-iron cylinders fitted with stirrers and heated with hot air. The usual charge is 700 lbs. caustic soda (70 p.c.) dissolved in water, 1,300 lbs. of a concentrated solution of 'soda salt,' and 13 to 15 p.c. of potassium chlorate, the amount of this latter substance varying slightly with the nature of the salt used, the monosulphonic salt requiring more chlorate than the disulphonic salt.

The temperature is kept up to about 180° for at least twenty-four hours and often much longer, the progress of the decomposition being controlled from time to time by extracting small quantities of the melt and examining them in the laboratory.

The product thus obtained is an intense purple fluid, becoming thick on cooling and containing the colouring matter as sodium salt besides sodium sulphite and an excess of caustic soda.

To separate the colour the melt is run into large wooden tanks, diluted with water, and boiled with dilute sulphuric acid.

This causes the solution to become orange in colour owing to the precipitation of artificial alizarin.

After being allowed to settle, the supernatant liquor is run off, the alizarin forced into filter presses and carefully washed until free from acid and saline matter. The colouring matter is then made up to a definite strength (10 p.c. or 20 p.c. paste as required) by transferring it to large wooden tubs fitted with powerful stirrers, and thoroughly mixing it with water.

Pure alizarin thus prepared produces a blue shade of Turkey-red, and anthrapurpurin (produced by fusing sodium anthraquinonedisulphonate with caustic soda) a red shade, so that by varying the amounts of these two constituents any intermediate shade required by the market can be obtained.

2. *Dichloranthracene process.*—In manufacturing alizarin by this process it is necessary, in the first place, to purify the anthracene used



much more thoroughly than is the case in the anthraquinone process.

For this purpose the anthracene after washing with petroleum spirit, as described in the last process, is submitted to distillation with potash. This removes the carbazol and the phenolic substances present in the crude anthracene, and as, besides this, a considerable quantity of the other impurities are charred during the distillation, the anthracene resulting, although still very impure, is found to be greatly improved in quality.

In carrying out this operation 100 parts of washed anthracene, 30 parts of potash, and 6 parts of powdered lime are thoroughly ground together under edge-runners, the mixture introduced into iron retorts and distilled. The distillate, which consists of pale-yellow cakes containing about 50 p.c. of pure anthracene, is now sufficiently pure for conversion into dichloranthracene.

In chlorinating anthracene, leaden chambers are used, technically known as 'chlorine ovens.' These are 10 ft. long, 4 ft. 6 in. wide, and 1 ft. 6 in. deep, and are used in pairs, connected at one end in order that any chlorine escaping from the first oven may come in contact with a fresh amount of anthracene and thus prevent loss.

400 lbs. of anthracene are put into each oven, and subjected to the action of a rapid current of chlorine for about five or six hours.

The anthracene first fuses and gets dark in colour, hydrochloric acid being evolved in abundance; but after a time this fluid product begins to deposit crystals and soon becomes a semi-solid mass. In order to purify this crude product, it is first freed from hydrochloric acid by washing with dilute caustic soda, and then pressed between linen cloths in a hydraulic press, by which means a considerable quantity of a thick dark oily product technically known as 'chlorine oils' is got rid of.

The yellow cakes of dichloranthracene thus obtained are still not pure enough for use, they must next be soaked in coal-tar naphtha for some time and pressed, this operation being repeated until a product is obtained which contains 84 p.c. of pure substance.

The next process consists in converting the dichloranthracene into the sulpho-acids of anthraquinone by treating it with ordinary concentrated sulphuric acid. This decomposition is accomplished in iron pots capable of holding about 30 gallons and fitted with iron covers in which there is an opening for the escape of the acid vapours formed during the reaction.

These pots are charged with 350 lbs. of concentrated sulphuric acid and heated to 140°-160° by means of an ordinary fire, the dichloranthracene (70 lbs.) being shovelled in in small quantities at a time. After all the dichloranthracene has been added and the frothing due to the evolution of the hydrochloric and sulphurous acids produced during the decomposition has subsided, the temperature is gradually raised to 260° and then maintained at this point until a sample taken out on a glass rod and diluted with water forms a nearly clear solution devoid of fluorescence.

The product contains now the mono- and disulphonic acids of anthraquinone, the latter of which greatly predominates.

These crude sulphonic acids are next diluted with water in a large wooden tank and boiled with slaked lime until neutralised. The neutral product is then forced into filter presses to separate the calcium sulphate, the clear filtrate mixed with the washing of the calcium sulphate, evaporated until it contains about 15 p.c. of lime salts, and then treated with sufficient sodium carbonate to precipitate all the lime as carbonate.

The solution of the sodium salts of the sulphonic acids is siphoned from the precipitated calcium carbonate, concentrated until it contains 30 p.c. of soda salts, and then converted into colouring matter by fusion with caustic soda, as described in the last process. W. H. P. jun.

**ALIZARIN BLUE** v. ALIZARIN AND ALLIED COLOURING MATTERS.

**ALIZARIN ORANGE** v. ALIZARIN AND ALLIED COLOURING MATTERS.

**ALKALI ALBUMIN** v. ALBUMINOIDS.

**ALKALI BLUE.** *Nicholson's blue.* Sodium triphenyl-rosaniline sulphonate v. TRIPHENYL METHANE COLOURING MATTERS.

**ALKALI GREEN** or **VRIDINE**, Sodium diphenyldiamido-triphenyl carbinol sulphonate  $C_{31}H_{23}N_2SO_3Na$ , a colouring matter obtained by Meldola in 1877 by acting on diphenylamine with benzyl chloride, oxidising the benzyl diphenylamine and sulphonating the resulting product. Dark-green powder, soluble in water; solution gives a green precipitate with HCl; a brown coloration with caustic soda, and a fuchsin-red solution with  $H_2SO_4$ .

**ALKALIMETRY** v. ACIDIMETRY.

**ALKALI WASTE** v. SODA MANUFACTURE.

**ALKANET.** *Alkanna. Anchusine.* This term is applied to two different plants, viz. *Lavosonia inermis* (v. AL-KENNA) and *Anchusa tinctoria*. The latter, or *False alkanet*, is also known as *Orkanette*, Fr.; *Orkanet*, Ger.; *Languedoc bugloss* or *Dyers' bugloss*, *Radix alkanne spuria*. A rough plant with downy spear-shaped leaves, and clusters of purplish or reddish flowers, belongs to the *Boraginaceae*. Figured in Girardin's *Chimie*, 4, 277. Found in Asia Minor, Greece, Hungary, &c. The roots, which have an astringent taste, occur in commerce, varying from the thickness of a quill to that of a finger. They give up their colouring matter to oils, fats, waxes, spirits, &c., by simple infusion. The dye may be isolated by extracting with water, drying, and digesting the residue with alcohol; the extracts are concentrated, shaken with ether, and the ethereal extract evaporated. Thus obtained anchusine is an amorphous substance of a deep-red colour, which softens at 60°C., dissolves in ether, oil, and acetic acid, but is only slightly soluble in water. Its composition is variously given as  $C_{17}H_{16}O_4$  (Pelletier, A. 6, 27),  $C_{15}H_{12}O_8$  (Bolley and Wydlers, A. 62, 41), or  $C_{17}H_{14}O_4$  (Carnelutti and Nasini, B. 13, 1514).

Used by druggists and perfumers to colour tinctures, oils, pomades; by varnish makers to tint their varnishes; by statuarics for tinting marble; by dairy farmers for colouring cheese; and by wine merchants for dyeing corks and colouring artificial wines. Dyes cottons, mordanted with iron, grey; with aluminium, lilac violet; but the colours are not fast (Girardin's *Chimie*, 4, 279).

Its absorption spectrum shows three bands dividing the spectrum between v and the blue

strontium line into four equal parts. On adding ammonia the red solution turns blue, and shows two bands, one at D, the other in the red two-thirds of the way towards the lithium line (Dupré, C. J. 37, 572). The absorption spectrum varies slightly, according to the solvents and salts present.

Böttger (J. pr. 107, 146) and Enz (J. 70, 935) recommend the use of papers dyed by alkanet as indicators in alkalimetry.

According to John the percentage of anchusine in the root is 5.50. Thompson (Ph. [3] 16, 860) found that it varies from 5.50 to 6.02 p.c.

For the detection of alkanet in wines v. Herz (Rep. Anal. Chem. 5, 210; S.C.I. 5, 30).

**AL-KENNA.** The powdered roots and leaves of the *Lausonia inermis* used in the East for dyeing the nails, teeth, hair, and garments. Used in Persia mixed with lime for dyeing the tails of horses.

**ALLEMONTITE.** A native alloy of arsenic and antimony,  $SbAs_3$ , found at Allemont in the Dauphiné, Prajbram in Bohemia; and Andreasberg in the Hartz.

**ALLOCLASE.** A mineral, formerly regarded as cobalt glance, crystallising in rhombic prisms. Hardness, greater than 4. Sp. gr. = 6.6. Tschermak (W.A.B. [3] 1, 1; J. 1836, 918) gives it the formula  $Co_3As_2S_6$ .

Frenzel (Min. Petr. Mitth. [2] 5, 179; J. 33, 1831) has analysed six specimens from the Elizabeth pit, Oravicza, with the following results:—

Bi	Cu	Co	Fe	As	S	Ant	Sp.gr.
22.68	0.16	19.90	2.66	27.74	15.60	1.19	6.23
	to	to	to	to	to	to	to
32.27	0.45	24.20	3.80	32.64	13.14	1.70	6.50

**ALLOMORPHITE.** A mineral from Rudolstadt, consisting mainly of barium sulphate (Gerngross).

**ALLOYS.** Since many valuable mechanical properties are conferred upon metals by associating them with one another, it seldom happens that when metals are devoted to industrial use they are used in a state of purity, and this fact was discovered at a very early period of metallurgical history. In all probability the word 'alloy' originally comes from the Latin *ad-ligo* (*alligo*) 'to bind to.'

Throughout the whole of the Middle Ages there seems to have been a belief that the action of a base metal on a precious one was, on the whole, corrupting, and Biringuccio, in 1540, probably gave the true definition of alloys, which were, he said, nothing but 'intimate associations of metals with one another,' and he pointed out that metals must be 'mixed by weight and not at random.' In early times some metals were used unalloyed, although at the present day they have no industrial application except in union with other metals. Antimony, for instance, now only employed as a constituent of certain alloys, was formerly cast and fashioned into ornaments, as is proved by the analysis by Virchow, and by a fragment of a Chaldean vase, which when examined by Berthelot was found to be of pure antimony (A. Ch. Sept. 1837, p. 135). The implements and ornaments discovered by Schliemann abundantly show that the early Greeks were familiar with alloys of silver and gold, copper and tin, lead and silver, and many others, all artificially prepared.

Without attempting to give the history of research connected with alloys it may be mentioned that in the period from the sixteenth to the eighteenth centuries there were four writers whose names deserve to be specially remembered because they seem to have been the first to indicate the direction in which modern investigation has been conducted. These are Réaumur, Gellert, Musschenbroek, and Achard, who respectively studied:—(1) Réaumur—molecular change produced in a metal by heat; (2) Gellert—the relation of fluid metals to each other considered as solvents; (3) Musschenbroek—the cohesion of alloys as shown by certain mechanical properties; and (4) Achard—the electrical behaviour of metals and alloys.

Réaumur (*L'Art de convertir le fer forgé en acier*, Paris 1722, p. 321), in explaining the hardening of steel by rapid cooling from an elevated temperature, comes very near the modern view that a metal may assume an allotropic state, for he distinctly contemplates the possibility of molecular change produced by the expulsion by heat of 'sulphurs and salts' from the molecules into interstitial spaces between them, as he speaks of molecules and the elementary parts of molecules like a modern writer, and tries to show that when hot steel is rapidly cooled, 'sulphurs and salts' cannot re-enter the molecules, but remain in the interstitial spaces, and therefore the physical properties of hard steel become quite different from those of the soft metal. That this analogy between carburised iron and alloys is not overstrained is shown by the fact that in 1867 Matthiessen, after appealing to the fact that in certain alloys metals are in allotropic states, said 'I have always made a comparison between iron and steel (and alloys). This has been done to show that the carbon iron alloys behave in an analogous manner to other alloys which cannot be looked upon as chemical combinations' (Lecture delivered before the Chemical Society, Journal, 1867, p. 220). Gellert makes the analogy of certain alloys to solutions very clear, and in his *Metallurgic Chemistry* he gives a table showing the relative solubilities of metals in each other, while in the observations which accompany it he says (English translation of his work, London, 1766, p. 186), to take one instance as an illustration, 'Since copper and silver, and copper and gold, dissolve one another very readily, the copper cannot be parted from iron by means of gold or silver,' as copper could be parted from gold by the addition of sulphur, and he further clearly shows that with regard to the solution of metals in a triple alloy he understood the possibility of the division of a metal between two other metals acting as solvents.

Musschenbroek, who worked in the first part of the eighteenth century, made some very early experiments on the tensile strength of metals and alloys. He writes of the 'absolute cohesion by which a body resists fracture when acted upon by a force drawing according to its length' (*Elements of Philosophy*, translated by John Colson, F.R.S., 1744, vol. 1, p. 237). He gives the tenacity of several metals, and of the alloys brass and pewter.

Achard, whose results were published in 1784, made a very extended series of experi-



ments on multiple alloys as well as on those of simple metals. He pointed out that the relative conductivities of substances for heat and for electricity are exactly related. He devised an appliance for the experimental verification of this fact, and as he included alloys in his investigations it may fairly be claimed that he led the way for the important generalisation made by Wiedemann and Franz in 1853, that in alloys the order of conductivity for heat and for electricity is the same.

The importance of metals being pure when added to each other was hardly recognised until the eighteenth century, and Duhamel, who contributed the article on Alloys to the *Encyclopédie Méthodique* in 1792, appears to have been the first writer to insist on the necessity for making exact experiments upon alloys with metals which possess a high degree of purity, and on effecting their union by heat in closed vessels. He added that up to his time no chemist had taken these precautions, and it is certain that in conducting some modern experiments they have been neglected.

The early researches, properly so called, on alloys were directed to ascertaining the effect on the specific gravity of metals produced by alloying them, and to determining the effects of slowly cooling alloys possessing low melting-points. The work of Ermann (P. 9, 557) in 1827, and of Rudberg (P. 18, 240), was of such a nature. Ermann called attention to certain anomalies in solid alloys, Rudberg to anomalies in alloys when in the liquid state.

Regnault showed that the specific heats of alloys are greater near  $100^{\circ}$  than the mean specific heat of their constituents, and this fact appears to have induced Person to undertake researches on the latent heats of alloys and on their specific heats. Undoubtedly one of the greatest works on alloys of the present century was that of Matthiessen (Tr. 1860, 85, &c.) who investigated the electrical resistance of metals and alloys, and who was led to the conclusion that the electrical conductivity of the alloys of any two metals may be represented by one or other of three typical curves:—U-shaped, as in the case of gold-silver alloys; L-shaped, as in the case of the copper-tin series; and nearly a straight line, as in the case of the lead-tin alloys. Not the least important conclusion arrived at by Matthiessen was that, in certain alloys, the constituent metals exist in allotropic forms. With regard to the influence of the passage of an electric current through *molten alloys* the evidence is so far of an uncertain nature. Obach (P. Sup. 7 (1876), 280) in examining this question did not confirm Gérardin's statement (C. R. 43, 727) that liquid amalgams and alloys undergo electrolytic decomposition on the passage through them of an electric current; and Roberts-Austen failed to produce any change in fused lead-gold or lead-silver alloys by passing through them a current of 300 ampères from secondary batteries (B. A. 1887, 341). The experiments seem to show that the passage of a strong current through a fused alloy does not effect any change in its composition, and the question now arises: Is there a group of bodies between true alloys and true electrolytes in which some gradual change from metallic to electrolytic con-

duction can be proved to occur? That this may possibly be the case is incidentally supported by the evidence afforded by Hittorff (P. 1851, 84, 14), who shows that while the sulphides of silver and copper ( $\text{Cu}_2\text{S}$ ) conduct metallically at ordinary temperatures, they suffer electrolytic decomposition when the temperature is somewhat increased.

**Properties of Alloys.** *Liquation.*—When a fused alloy separates on cooling into two or more alloys of different density, or of different fusibility, or when from a solid alloy one or more of the constituents, possessing a lower melting-point than that of the remainder, is separated by the aid of heat, this phenomenon is termed liquation. It is of considerable metallurgical importance, being used for the purification of impure metals. Of the *copper-tin* alloys, those possessing the compositions represented by the formulæ  $\text{Cu}_3\text{Sn}$ ,  $\text{Cu}_2\text{Sn}$ , and  $\text{Cu}_7\text{Sn}_2$  are stated to show no tendency to liquation. The *copper-zinc* alloys either do not liquefy at all or only to a very slight extent. The *copper-lead* alloys liquefy to such an extent that the two metals may be almost completely separated from each other. Of the *silver-copper* alloys, only that with 71.9 p.c. of silver is homogeneous. The *tin-zinc* and the *lead-silver* alloys show a great tendency to liquation.

*Density.*—The specific gravity of an alloy is rarely the same as the mean of those of its constituents; it is usually either more or less than that calculated from the percentage composition. In the case of the *copper-tin* alloys, the specific gravity decreases with the increase in the percentage of tin, until this reaches 28 p.c.; when the percentage exceeds this, the specific gravity is greater than the calculated mean until the alloy containing 38.3 p.c. of tin— $\text{SnCu}_3$ —is reached, the specific gravity of this alloy exceeding that of copper itself. Beyond this point the specific gravity diminishes again. In the *copper-zinc* alloys a considerable increase of density is observed in those containing from 40.80 p.c. of zinc. The whole of the *copper-silver* alloys show a lower actual specific gravity than that found by calculation. The specific gravity of the alloys of the copper-gold series varies irregularly; usually it is almost identical with that calculated. All the *lead-gold* alloys show increased specific gravities; the specific gravities of the *lead-silver* alloys are less than the calculated ones, until starting from lead with a trace of silver the alloy with 11.5 p.c. of silver is reached; beyond this point the difference diminishes, and those alloys with more than 34 p.c. of silver show increased specific gravities. The specific gravities of the alloys of *antimony-bismuth*, and of *tin-cadmium* containing less than 75 p.c. of tin, are almost identical with those found by calculation.

*Tenacity.*—By alloying metals together, their tenacity is sometimes increased and sometimes diminished; usually, however, it is increased.

*Hardness.*—This is almost always increased.

*Extensibility.*—Almost always diminished.

*Fusibility.*—The melting-point of an alloy is usually less than the arithmetical mean of the melting-points of the alloyed metals.

*Expansion by heat.*—The coefficients of expansion of alloys frequently differ considerably



from that found by calculation; this variation is, however, irregular.

**Colour.**—The alloys showing the greatest variation of tint are those of copper and of gold. The only alloy possessing a violet colour is the 'Regulus of Venus,'  $\text{Cu}_2\text{Sb}$ .

Among the more important recent researches in connection with alloys, those of W. Spring deserve special mention, as he has thrown much light on their molecular constitution by proving that they can be built up from the powders of the constituent metals by simple pressure (Bull. Acad. Roy. Belg. [2] 45, No. 6, 1878; 49, No. 5, 1880, &c.). Hallock (Z. P. C. 2, 378) finds that alloys may be formed from their components without extra pressure provided the temperature be above the melting-point of the alloy itself. In a more recent research on the lead-tin alloys (Bull. Acad. Roy. Belg. [3] 11, 1886, No. 5) Spring, from thermal considerations, comes to the same opinion as that of Matthiessen concerning the possibility of alloyed metals assuming allotropic forms.

The industrial importance of the influence exerted by small quantities of metallic and other impurities on masses of metal in which they are hidden is now becoming fully recognised. With regard to gold some researches made by Hatchett (P. T. 1803) have recently been repeated by Roberts-Austen (P. T. 179, 1888, A. 339), who by determining the influence of impurities on the tenacity and extensibility of gold comes to the conclusion that their action is controlled by the periodic law. He shows that an element with a larger atomic volume than gold greatly diminishes both its tenacity and its extensibility, whilst an element with a smaller atomic volume tends to improve these qualities.

'Alloys used for coinage' have been very fully dealt with by the Chemist of the Mint in the Journal of the Society of Arts, 1884, and a comprehensive bibliography of alloys is given in Ledebur's *Metallverarbeitung*, Brunswick, 1882.

W. C. R.-A.

**ALMAGRERITE.** Native anhydrous zinc sulphate, found in crystals belonging to the rhombic system at Barranca Jarosa Mine, Sierra Almagrera, S. Spain (Breithaupt).

**ALMASCA.** A soft grey resin soluble in chloroform, ether and absolute alcohol. Probably derived from *Icica heptaphylla* (Symes, Ph. [3] 13, 213).

**ALMIRAO.** Indian name for *Microrhynchus sarmentosus* used at Goa as a substitute for taraxacum (Dymock, Ph. [3] 6, 730).

**ALOE.** A genus of succulent plants, having stiff, pointed, fleshy leaves, belonging to the Liliaceæ. (Plants figured, and structure of leaves described, Pennetier, 560, 579.) They are natives of the tropics. (For a list of the species and their distribution, v. Ph. [3] 11, 746.)

The fibre is used for rope, &c.; experiments made in Paris have shown it to be five times as strong as hemp. The fibre has also been used for paper-making (Nat. 20, 484).

**ALOE RESIN.** Separates from solutions of aloes in boiling water; according to Kossmann, has the same composition as aloin. On treatment with sulphuric acid it gives glucose, aloëresinic acid  $\text{C}_{15}\text{H}_{10}\text{O}_8$ , and aloëretinic acid  $\text{C}_{15}\text{H}_8\text{O}_8$  (Kossmann, J. Ph. [3] 40, 177).

**ALOE8 or BITTER ALOE8.** *Aloë8*, Fr.; *Aloë*, Ger. The inspissated juice or extract of the aloë. The principal varieties found in the market are:—

1. *Barbadoes Aloes* (aloes in gourds). The juice of *A. vulgaris* and *A. sinuata* growing in Barbadoes, Jamaica, and St. Helena. It is opaque, lustreless, and of a brown colour, with a bitter nauseous taste and very disagreeable odour; it gives a powder of a dull-yellow colour.

2. *Cape Aloes* (*Aloe capensis*, *A. lucida*), obtained from *A. spicata*, *A. africana*, *A. ferax*, and other Cape species. Its odour is stronger and more disagreeable than that of Barbadoes aloes; it is of a deep greenish-brown colour, is resinous and shining, and its powder is of a greenish-yellow colour, and is almost completely soluble in boiling water.

3. *Hepatic Aloes*. Imported from Bombay and Madras. It is probably the juice of the Socotrine aloë solidified without the aid of artificial heat (Pereira, Ph. [3] 11); it is of an opaque liver colour, its powder contains much matter insoluble in weak alcohol.

4. *Socotrine Aloes*. The juice of *A. Perryi* (Baker) imported from Bombay and Madras. It is of a garnet-red to golden-red colour, is aromatic, and has an intensely bitter taste; its powder is of a bright golden yellow colour (Cooley, 1).

5. *Zanzibar Aloes* from Zanzibar.

By extracting aloes with water the purgative principles, aloins, can be obtained. Shenstone (Ph. [3] 13, 461; C. J. [2] 44, 80) divides them into two classes:—

1. *Nataloins*, which only yield picric and oxalic acids with nitric acid, and which are not reddened by it, even on heating (Flückiger, Ar. Ph. [2] 149, 11; Tilden, C. J. [2] 10, 153).

2. *Barbaloins*, which yield aloëtic acid  $\text{C}_8\text{H}_2\text{N}_2\text{O}_5$ , chrysammic acid  $\text{C}_8\text{H}_2\text{N}_2\text{O}_5$ , picric and oxalic acids, and are reddened by nitric acid.

*a*-*Barbaloins* from Barbadoes aloes reddened in the cold by strong nitric acid (Tilden, Ph. [3] 2, 845; C. J. [2] 10, 488).

*β*-*Barbaloins* from Socotrine, Zanzibar, and Jaffierabad aloes, coloured only on heating with ordinary, and in the cold with fuming, nitric acid (Flückiger, *l.c.*; Tilden, C. J. [2] 28, 270; Ph. [3] 4, 208).

Nataloin,  $2\text{C}_8\text{H}_2\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ , was discovered in 1856 by Groves. It crystallises in bright-yellow scales, melts at  $212^\circ\text{C}$ .– $222^\circ\text{C}$ ., and is soluble in water, benzene, carbon disulphide, chloroform, and ether. It is soluble in concentrated sulphuric acid, the addition of a crystal of potassium nitrate producing a characteristic bright-green colouration passing rapidly from red to blue. Chromic acid oxidises it to carbon dioxide, acetic acid, and probably quinone (Tilden, Ph. [3] 8, 231; C. J. [2] 32, 264, 903).

Barbaloin,  $\text{C}_{15}\text{H}_{10}\text{O}_8$ , was isolated by Smith (Chem. Gaz. 1851, 107) and analysed by Stenhouse. It crystallises in yellow prismatic needles, which, on fusion with caustic potash, yield orcin, *p*-hydroxybenzoic, and aloeic acids (Hlasiwetz, A. 134, 237; 136, 31). Barbaloin and socaloin, on oxidation with chromic acid, break up into carbon dioxide, acetic acid and alloxanthin,  $\text{C}_{15}\text{H}_3(\text{Me})(\text{OH})_2\text{O}_2$  (Tilden, Ph. [3] 8, 231; C. J. [2] 32, 264, 903).

Schmidt (C. J. 1876, 2, 641; Ar. Ph. [3] 6, 496-509) obtained a body to which he assigned the formula  $C_{15}H_{15}O_5$ , by extracting Barbadoes aloes with dilute sulphuric acid. Zanzaloin,  $C_{44}H_{48}O_{15} + 5H_2O$ , discovered in 1871, crystallises in tufts of yellow needles.

By the action of sulphuric acid upon aloin, glucose and rottlerin are formed, according to Czumpelik (J. 1861, 743), Rochleder (*ib.* 598); glucose, aloëresic acid  $C_{30}H_{32}O_{11}$ , aloëretin  $C_{30}H_{32}O_{11}$ , and aloëretic  $C_{30}H_{34}O_{11}$ , according to Kossmann (Bl. Chem. 63, 389), whilst Hlasiwetz states that *p*-coumaric acid is formed (A. 131, 287; 136, 31); *p*-coumaric acid was also obtained by Rochleder and Czumpelik (J. pr. 84, 436) by boiling aloin with a solution of caustic potash.

By distilling, a yellowish oil, sp.gr. 0.877, boiling-point  $130^{\circ}C$ ., was obtained by Robiquet (J. Ph. [3] 10, 167, 241), which Rembold (A. 138, 186) regards as a mixture of xylyl alcohol, acetone, and hydrocarbons.

Graebe and Liebermann (Z. [2] 4, 503) obtained anthracene by distilling aloin with zinc-dust.

*Uses*.—Chiefly in medicine and as a hop-substitute. It has also been used as a source of certain dyeing materials (Ure, 1, 101; Preston, C. C. 1876, 390; C. J. [2] 32, 378). Kayser (Chem. Tech. Repert. 1876-80) finds aloë colouring matters make the aniline dyes, e.g. fuchsins, faster.

*Properties and Reactions*.—Pure aloes is soluble in ether and almost completely soluble in water, the solution being coloured dark-brown by alkalis, black by ferric chloride, and grey by plumbic acetate (Flückiger). By adding a solution of copper sulphate or chloride to a solution of aloes, an intense yellow-coloured solution is obtained, which, warmed with bromide or chloride of potash, turns to a deep-red and reddish-violet tint (Klunge, B. 16, 1691; Ar. Ph. 1883, 363). Bornträger (Fr. 19, 165; B. 13, 1040) extracts with twice the volume of benzene, and adds to the clear extract a drop of ammonia, when, on warming and shaking, the solution becomes violet-red; Groves (Ph. [3] 11, 1045) finds that this colour is not due to aloin, but probably to a tannin-like substance. Lenz (Fr. 21, 220) extracts with amyl alcohol, evaporates the extract, treats with nitric acid, and then with potassium cyanide and hydroxide, when a blood-red colouration is obtained.

Cripps and Dymond (Ph. [3] 15, 633) test for aloin by dissolving 1 grain in 16 drops of strong sulphuric acid, then adding 4 drops of nitric acid (1.42) and 1 ounce of water, when a deep orange or crimson colour is produced, deepened by ammonia; substances containing chrysophanic acid behave in a similar manner, but their aqueous solution turns pink upon the addition of ammonia.

**ALOE, ESSENTIAL OIL OF.** A pale-yellow mobile liquid to which the odour of aloes is due. Sp.gr. 0.863, boils  $266^{\circ}$ – $271^{\circ}$ . It exists in very small quantities in the aloes, and when pure has the taste and smell of oil of peppermint (Ph. [3] 10, 613).

**ALOE WOOD.** A name applied to the wood of *Alseodryon agallochum*, a leguminous tree of Cochin China, and to that of *Aquilaria agallochum* and *A. ovata* of tropical Asia. Both are

highly fragrant and aromatic; used in fumigations and pastilles, and occasionally by cabinet-makers and inlayers.

The same name is applied to the resin. Of all perfumes this is said to be the most esteemed by Orientals (Cooley).

**ALOE BOKHARA, ALPOGADA, PAZHAM.** The Bokhara plum (*Prunus Bokhariensis*), largely imported into Bombay. Used as a laxative. The root is astringent; the gum is used as a substitute for gum arabic under the name of Persian gum (Dymond, Ph. [3] 9, 145).

**ALOUCHI RESIN** v. *Aluchi Resin*, art. RESIN.

**ALPOGADA** v. **ALOE BOKHARA**.

**ALQUIFON.** Black lead ore or Potters' ore. A native lead sulphide, used by potters to give a green glaze to coarse wares (Cooley).

**ALSTONIA BARK.** The bark of *Alstonia constricta*, an apocyanaceous tree growing in Australia. It has a bitter taste, slightly camphorous odour, contains a neutral bitter principle (similar to cailcedrin and tulucumin), a volatile oil smelling like camphor, an iron-greening tannin, resin, fat, wax, a protein-like substance, oxalic and citric acids (Palm, J. 1863, 615).

Müller a. Rummel (C. J. [2] 35, 31) obtained a yellow substance to which they gave the name *alstonine*. Oberlin a. Schlagdenhauffen (Ph. [3] 10, 1059; C. J. [2] 38, 127) showed that this body consisted of two compounds *alstonine* and *alstonicine*, the former being soluble in acids with fluorescence, the latter without.

Hesse subsequently (B. 14, 264; A. 205, 360; Ph. 11, 775; C. J. [2] 40, 623) isolated:—

*Alstonine* (chlorogenine)  $C_{20}H_{21}N_2O_4$ , a brown amorphous mass, a strong base, soluble in chloroform, alcohol, and sparingly soluble in ether, and melting when anhydrous at  $195^{\circ}C$ . (uncor.).

*Porphyryne*,  $C_{21}H_{23}N_3O_2$ , a white powder melting at  $97^{\circ}$  (uncor.), soluble in alcohol, chloroform, ether and acids with blue fluorescence.

*Porphyrosine*, soluble in acetic acid, forming a pink solution.

*Alstonidine*, colourless needles, melting at  $181^{\circ}C$ . (uncor.), soluble in chloroform, ether, alcohol and acetone.

Hesse, however, could not find a trace of quinine (B. 11, 1546, 1753; C. J. [2] 36, 269).

**ALSTONIA SPECTABILIS.** *Poëlle bark*. Contains *alstonamine* (Hesse, B. 11, 1548; C. J. [2] 36, 71), and the alkaloids of dita bark. It contains six times as much echitanium hydroxide as dita bark (Hesse, A. 203, 144; Ph. [3] 11, 251).

Its physiological action is like that of curare.

**ALTI.** Indian name for a root used at Goa as a substitute for Althaea (Dymond, Ph. [3] 8, 101).

**ALUDEL.** The aludels of the earlier chemists were pear-shaped pots generally made of earthenware, but sometimes of glass, open at both ends. Each aludel had a short neck at the top and bottom, so that a series of them could be fitted together by means of the necks. The earthenware pear-shaped vessels in which the mercurial vapours are condensed at Almaden in Spain are also known as aludels; v. MERCURY.

**ALUM** v. **ALUMINIUM**.

**ALUMINATES** v. **ALUMINIUM**.

**ALUMINIUM.** Sym. Al. At. w. 27.04 (Mallet, Berzelius, Tissier, Dumas, Isnard, Terreil, Baubigny).

*Occurrence.*—Aluminium is the most widely distributed element in nature with the exception of oxygen and silicon, with which it usually occurs in combination. It is not found in the metallic state.

As oxide  $Al_2O_3$ , aluminium is found in *corundum*, or, coloured by metallic oxides, in *sapphire*, *ruby*, *emery*, &c. The hydrated oxide  $Al_2O_3 \cdot H_2O$  occurs as *diaspore*, and, together with ferric oxide, as the important mineral *baurite*.

Aluminium occurs in combination with oxygen and metals as *aluminates*, in *spinel*  $Al_2O_3 \cdot MgO$ , *chrysoberyl*  $Al_2O_3 \cdot BeO$ , *gahnite*  $Al_2O_3 \cdot ZnO$ . As hydrated sulphate it is found in *aluminite* or *websterite*  $Al_2O_3 \cdot SO_4 \cdot 9H_2O$ , and as *alunogen*  $Al_2O_3 \cdot SO_4 \cdot 18H_2O$ ; as the double sulphate of aluminium and potassium in *alumstone* or *alumite*; and, as an efflorescence on aluminous minerals, as the alums of potassium, sodium, ammonium, &c.

Aluminium occurs principally, however, as silicate in the various *clays*; as silicate containing silicon fluoride in the *topaz*, and, as double silicate, with iron, magnesia, lime, &c., in *garnets*; with potassium, sodium, magnesium, and calcium in immense quantities in the varieties of *felspar*.

As double fluoride of aluminium and sodium it is found in *cryolite*  $AlF_3 \cdot 6NaF$ ; as hydrated phosphate in the *turquoise* and in *wavellite*, and as borate in a crystalline mineral occurring in Siberia.

Although present in such quantities in the soil, aluminium is not usually considered a constituent of the ash of plants except of cryptogams; Yoshida, however (C. J. 1887, 748), has found it in a number of phanerogams in Japan.

*History.*—The name of this metal is derived from *alumen*, a term applied by the Romans to all bodies of an astringent taste. Pott, in 1746, stated that the basis of alum is an argillaceous earth; and in 1754 Margraff pointed out the distinction between alumina and lime, and its presence in combination with silica in clay.

Davy, in 1807, having isolated the alkali metals by electricity, endeavoured, unsuccessfully, to reduce alumina in the same manner.

An important advance was made by Oersted in 1824. He prepared aluminium chloride by passing chlorine over a mixture of alumina and carbon heated to redness. He appears to have reduced the chloride to the metallic condition by heating with potassium amalgam (Berzelius, Jahresb. 1827 [6] 118). The amalgam produced oxidised rapidly in the air, and left, on volatilising the potassium, a tin-white metal. An amalgam may be formed directly by heating a mixture of mercury and finely-divided aluminium, which is decomposed by contact with water.

Wöhler, in 1827 (A. 1828, 37, 66), having failed to procure the metal by Oersted's method, obtained it by the decomposition of the *anhydrous* chloride with potassium, as a grey powder, which became brilliant under the burnisher. In 1845 he obtained globules as large as a pin's head; first, by heating a mixture of potassium and aluminium chloride, and,

later, on account of the violence of the action, by the method also adopted by Liebig, of passing the vapour of the chloride over heated potassium. The metal so obtained showed, however, properties very different from those of pure aluminium, and doubtless contained potassium and aluminium chloride, and also platinum, when vessels of that metal were used in the preparation.

Bunsen and Deville, in 1864, independently, obtained the metal by electrolysis of the fused chloride. Deville, in the same year, much simplified the manufacture by substituting sodium for the more expensive potassium. In 1854 he was installed in the manufactory of Javel by the Emperor Napoleon III., and supplied with the necessary apparatus for experiments on the large scale. A description of his method is given in A. Ch. [3] 43, 5-36, and specimens of the metal produced were shown at the Paris Exhibition of 1855.

Shortly after the publication of these results, Messrs. Dick and Smith, under the direction of Dr. Percy, prepared aluminium by the action of sodium on the newly-discovered mineral *cryolite*, some of the product being shown by Faraday at the Royal Institution in March 1855 (P. M. 10, 365).

About six months subsequently, Rose, independently, prepared it in the same manner, and published his results in an extended article in P. 96, 152 (P. M. 10, 233).

Deville at once turned his attention to this process (A. Ch. [3] 46, 151); but on account of the impurity of the metal produced, he preferred the double chloride of aluminium and sodium, using cryolite as a flux only.

Wöhler (A. 99, 255) proposed a method for preparing aluminium free from silicon by this method in ordinary crucibles. It was adopted by Tissier Frères at Rouen, but was soon abandoned on account of the smallness of the yield.

The first manufactory in England was started at Battersea, London, in 1859, by F. W. Gerhard. Some of his metal was shown at the Society of Arts Exhibition in 1860. Messrs. Bell, of Newcastle, also prepared aluminium and aluminium bronze, but the manufacture has been discontinued.

Notwithstanding the large number of processes proposed during the last thirty years for its manufacture, practically the whole of this metal is at present produced by Deville's process at the manufactory of Salindres. Mr. Castner's process of manufacture, now in operation at the Aluminium Company's Works in Oldbury, promises, however, to reduce very considerably the cost of production.

*Manufacture.*—All attempts to produce aluminium by the reduction of its oxide, except, perhaps, by the use of electricity, have been unsuccessful. The affinity between this metal and oxygen increases considerably at high temperatures, as shown by its tendency to produce aluminates when heated to whiteness with certain metallic oxides and salts. This, together with its high heat of formation, renders it improbable that the oxide will be reduced by ordinary reducing agents at the temperatures at present available. Hitherto the haloid salts have been the source of the metal, the chloride and fluoride being used on the large scale.



These salts are rapidly reduced by the alkali metals. Sodium alone is used on account of its lower cost and less violent action than potassium.

The use of zinc has been recommended by many chemists for the reduction of the chloride. Dullo (Bl. 1860, 472), Basset (Le Génie Industriel, 1862, 152), Wedding (J. Ph. [4] 3, 155), and others have advised its use. According to Flavitzky (B. 6, 195), however, zinc chloride itself is reduced by *aluminium*.

Weldon (Eng. Pat. 1883, 97) states that the haloid salts may be reduced by *manganese*. Aluminium, however, appears to reduce manganese from its chloride.

The process adopted by Deville for producing the masses of aluminium shown at the Paris Exhibition in 1855 consisted in passing the vapour of aluminium chloride over heated sodium. The chloride was distilled from a vertical iron retort over a quantity of iron filings heated to dull redness. The ferric chloride and any hydrochloric acid present as impurity having thus become reduced, the vapour was passed through a tube cooled to about 300°C. where the ferrous chloride produced was deposited. The chloride passed thence into a chamber heated to dull redness, containing three iron dishes, each holding 500 grams of sodium. The chloride was rapidly reduced, and the sodium chloride produced combined with excess of aluminium chloride, forming a fusible mass of the double chloride containing globules of metallic aluminium. The action having ceased, the contents of the dishes were fused in a crucible, cooled, digested in water, and the metallic globules fused and pressed together with a clay rod.

Dewille also prepared the metal by passing the mixture of sodium vapour and carbon monoxide from a sodium generator into a large earthen crucible. As these gases ignited and heated the crucible, pieces of aluminium chloride were thrown in from time to time and reduced by the sodium vapour. This promising method produced very pure metal, but does not appear to have been successful on the large scale. A process not differing essentially from it has been patented by Frishmuth, of Philadelphia (U. S. Patent, 308, 152).

The yield of aluminium by these processes is far below the theoretical amount. This is explained by the fact that much of the metal is produced in a state of fine division, and is lost, partly mechanically, and partly by passing into solution during the washing. The chloride also is very hygroscopic, and appears to surround the globules of metal with a coating of oxide, which prevents them from uniting. The substitution of the much less hygroscopic double chloride of aluminium and sodium for the ordinary chloride considerably reduces this difficulty, but the addition of cryolite, or of fluorspar, renders it possible to obtain nearly the whole of the metal in one mass. This is due to the property possessed by fluorides of dissolving the film of oxide from the globules, and also to the great fluidity of the cryolite flux.

Cryolite may be reduced with facility by sodium, but the metal so produced is much less pure, on account of the solvent action of the

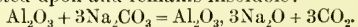
alkaline fluoride on earthen crucibles, and consequent introduction of silicon into the metal. When iron crucibles are used this impurity is avoided, but the metal then contains iron. For this reason cryolite is not used for the direct production of aluminium, but is invariably added as a flux.

For the following description of the preparation of aluminium on the manufacturing scale by M. Pechiney at Salindres, we are indebted principally to the account by M. Margottet in Frey's Encyclopædia, to Payen's *Chimie Industrielle* [1] 583, and to M. Wurtz in the Reports on the Vienna Exhibition of 1873 (Hoffmann's Ber. Entw. Chem. Indust. [1] 657).

The presence of a small quantity of iron in aluminium is very injurious. It is necessary, therefore, to use in the preparation only such substances as are free from iron. Aluminous minerals never occur in sufficient purity to be directly available, and require a preliminary treatment to remove iron before their conversion into the chloride. The preparation from bauxite consists of four distinct operations. (1) The formation of sodium aluminate. (2) Its conversion into alumina free from iron. (3) The production from the latter of the double chloride of aluminium and sodium. (4) The reduction of the chloride by sodium.

The bauxite preferred is obtained from the Department of Var, and contains usually 50 p.c.  $\text{Al}_2\text{O}_3$  and 25 p.c.  $\text{Fe}_2\text{O}_3$ . Of the finely-powdered mineral 480 parts are mixed with 300 parts of sodium carbonate. The mixture is strongly heated in a reverberatory furnace with frequent stirring until a portion no longer effervesces on addition of an acid. About five or six hours is usually required.

The alumina is thus converted into the soluble sodium aluminate, whilst the ferric oxide is unacted upon and remains insoluble:—



The apparatus used for the solution of the aluminate is of peculiar construction. A charge of 500 kilos (nearly half a ton) is placed within, upon a cloth filter stretched over a metal grating. The first wash-water consists of a weak solution of aluminate from the last washing of a previous quantity. It is conveyed through a tube from a separate vessel, over and through the mass, by a slight pressure of steam, and the whole is heated continuously by a steam jet. For the subsequent washings pure water is used. All liquors passing through of above 3°C. (1.02 sp.gr.) are mixed and produce 'strong liquor' of about 12°C. (1.085 sp.gr.).

The strong liquor has next to be treated for the re-production of the alumina, now entirely free from iron. It is placed in a closed vessel called a 'baratte' and subjected to the action of a current of washed carbon dioxide. The barattes are 2 metres long, 0.6 metres wide, and 0.8 metres high; each has a capacity of about 1,200 litres (264 gallons) and its contents are continually stirred by a mechanical agitator. A steam jacket at the bottom of the vessel maintains the temperature at 70°C. Three barattes are connected in series in order to utilise the whole of the carbon dioxide, and when the last fails to absorb the gas—usually after about five hours—the precipitation of the alumina in the

first may be considered complete. This is then emptied through a tap in the bottom, refilled and placed at the end of the series, so that the solution in which precipitation has most advanced is

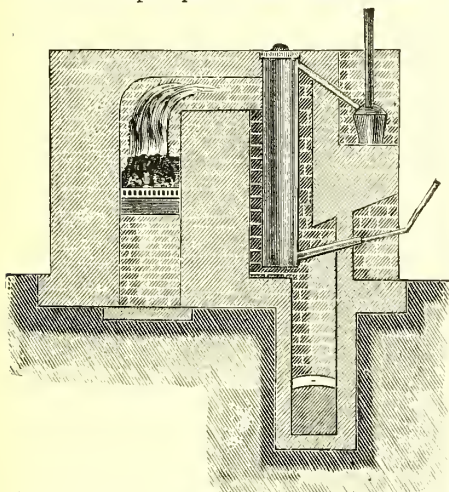
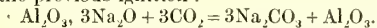


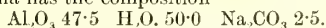
FIG. 1.

always first exposed to the gas. The chemical change is exactly the reverse of that occurring in the previous ignition :



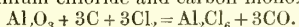
Nearly the whole of the carbonate used in the first instance may be thus recovered by evaporating the solution to  $32^\circ\text{B}$ . and crystallising.

The solution of carbonate having been decanted, the deposited granular alumina is freed from adherent liquid by means of a centrifugal machine and washed with water. A second rotation in the machine frees it sufficiently from carbonate for the next operation. The moist alumina has the composition



The dried alumina (100 parts) is mixed with salt (120 parts) and finely powdered wood charcoal (40 parts); the mixture is sifted to render it homogeneous, mixed with sufficient water to make it cohere, and the mass kneaded into balls about the size of the fist. They are dried at about  $150^\circ\text{C}$ . and transferred to a vertical cylinder of refractory earth (fig. 1), about  $1\frac{1}{2}$  metres high and 18 centimetres internal diameter, 6 or 8 such cylinders being arranged in each furnace. The cylinder cover is luted down with a mixture of fire clay and horse-dung and the whole heated gently until the balls are perfectly desiccated.

When this operation, which usually occupies a considerable time, is completed, the temperature is raised to redness and perfectly dry chlorine gas is passed through a tube in the lower portion of the cylinder. The gas passes through the porous balls, and, assisted by the action of the carbon, decomposes the alumina with production of aluminium chloride and carbon monoxide :



The chloride at once combines with the admixed salt producing the double chloride  $\text{Al}_2\text{Cl}_6, 2\text{NaCl}$ , which volatilises, passes through the tube in the upper portion of the cylinder and condenses in the earthen, flowerpot-shaped receiver as a

crystalline mass. The cover of this condenser is well luted on and supplied with a tube about 6 c.m. diameter through which the carbonic oxide passes into the chimney. The double chloride thus produced is very pure, and contains only a trace of iron. It is not removed from the condensers until required for use. During the first three hours the chlorine is almost completely absorbed and the double chloride distils regularly, but as the action proceeds the absorption is less complete, and the distillation is irregular. About 12 hours is occupied in each distillation, and the residue is removed after two operations. A retort lasts about a month.

The aluminium compound is now in the proper condition for reduction to the metallic state. A mixture of 100 kilos (220lbs.) of the double chloride and 45 kilos (100lbs.) of cryolite, all powdered, is divided into four portions. Three of these are mixed, each with 12 kilos ( $26\frac{1}{2}$  lbs.) of sodium in pieces about  $\frac{3}{4}$ -inch cube and placed in sheet iron baskets, the fourth portion, containing no sodium, is placed in a separate basket.

The reverberatory furnace used is of peculiar construction. It is built of refractory brick, and is so arranged that the flame may at any time be removed from the hearth; it is strongly built and braced by iron tie-rods to resist the concussions produced by the action. The furnace bed is about 80 centimetres long, and 50 centimetres wide in the middle. The bed and walls are well coated with a mixture of 4 parts calcined alumina and 1 part calcium aluminate to prevent as far as possible the introduction of silicon from the bricks into the metal. Towards the front of the bed is built a small brick wall, which may be removed when reduction is completed. A cast-iron gutter facilitates the running out.

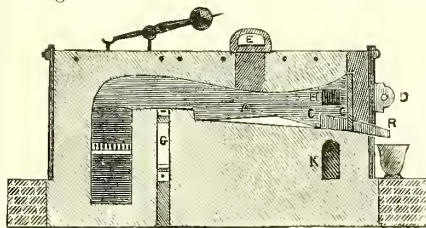


FIG. 2.

A. Slightly inclined bed of furnace. R. Iron gutter. C. Temporary wall. DD. Dampers. E. Opening for introduction of charge. HH. Communications with chimney.

The furnace is heated to redness, and the flame removed from the hearth. The material from the three baskets is rapidly inserted through an opening in the furnace roof, followed by the mixture containing no sodium, and the furnace entirely closed.

A violent action at once commences, with hard concussions on the side of the furnace. The reaction having subsided, the dampers are opened in about fifteen minutes, and the mass stirred with an iron poker. In three hours the reduction is complete, and the whole mass is in tranquil fusion with the metal beneath the slag.

The upper portion, or 'white slag,' is free from aluminium, and is removed by abstracting a brick from the upper portion of the temporary



wall. The metal is then run out from beneath the remaining slag by the removal of a plug from the bottom of the wall and received in a cast-iron pot previously heated to redness at the base. The metal is at once cast into small rectangular ingots. By two or three successive meltings the slag inclosed by the aluminium is eliminated.

The remaining slag is grey, and contains globules of aluminium. To facilitate its escape, the whole of the little wall is removed, and the slag is collected in the crucible in which the aluminium was received. It is allowed to cool gradually, and the small quantity of metal which collects beneath is removed.

In a good operation, 10·5 kilos of aluminium are produced from the quantities of material mentioned. According to Wurtz, 1,800 kilos of aluminium were produced at Salindres in 1872 at a cost for the various materials of:

1 kilo dry alumina . . .	0 fr. 50 c.
1 „ double chloride . . .	2 fr. 48 c.
1 „ sodium . . .	11 fr. 32 c.
Total cost of 1 kilo aluminium 80 fr.	

In 1882 the output had increased to 2,400 kilos per annum (Bull. Soc. de l'Industrie Minérale, 1882 [2] 451).

According to Weldon the comparative cost of the materials used at Salindres is:—Preparation of alumina, 9·67; conversion into double chloride, 33·4; additional cost for sodium, cryolite, &c. 56·93 (S. C. I. 1883, 368). From these figures it is evident that any radical change in the cost of production must depend on the reduction of the cost of the double chloride or of the sodium, or on the use of some other reducing agent or power.

The oxide prepared as already described is as pure as can be prepared by any process, and even a great reduction in the cost could but little affect the price of the metal.

By Castner's process (Eng. Pats. 1886, 7,395; 1888, 5,856) sodium is now being manufactured and sold at less than one-half its former price, whilst by his new process (Eng. Pat. 1883, 5,857) the cost of the double chloride is said to be reduced by one half.

Aluminium may also be produced by electrolysis of the fused haloid salts, preferably at a temperature a little below the melting point of aluminium.

According to Deville's method, the reduction may be performed in a porcelain crucible with a negative pole of platinum and a positive pole of carbon. When the double chloride of aluminium and sodium is used, aluminium and a little sodium chloride are deposited on the platinum, while chlorine and a little aluminium chloride are liberated at the carbon pole. The first portions of the deposit contain the greater part of the silicon and iron, so that by substituting a fresh platinum plate after a part of the metal has been deposited, very pure aluminium may be obtained. The current from two Bunsen cells is sufficient. The metal is detached, and fused under a layer of the double chloride.

Gore and many others have stated that it is possible to deposit aluminium from aqueous solution. None of these processes has, however, been successful, and Deville, Sprague, and

Winckler have particularly stated their inability to deposit the metal from solution. The action of alkaline solutions on aluminium would prevent the possibility of deposition from such liquids, and the same objection would apply to most neutral and acid solutions.

An electric furnace suitable for the production of very elevated temperatures was described by Dr. Siemens at Glasgow in 1881, and recently a furnace on somewhat similar principles has been patented by Messrs. Cowles Bros. for the reduction of alumina and other oxides (U.S. patents, 1885, 324,658, 324,659, 319,945, 319,795. Eng. Pat. (W. P. Thompson) 1885, 9,781; 1886, 1,160 and 1,161). The furnace is a rectangular box, one foot wide, five feet long, and fifteen inches deep, all inside measures. Two carbon electrodes pass through pipes in the ends; they are three inches in diameter and thirty inches long; this size cannot be exceeded, as larger carbons disintegrate under the intense heat. For a non-conducting furnace lining, fine particles of charcoal are washed in lime-water, exposed to the air and dried. They thus become coated with lime and are of good insulating power. At the high temperature produced, ordinary charcoal becomes converted into graphite and forms a good conductor. The two electrodes being within a few inches of one another, the charge of twenty-five parts of corundum, twelve parts of carbon and fifty parts of granulated copper is placed around and between them, covered with small lumps of charcoal, and the whole covered with an iron top lined with fire brick. The current from a powerful dynamo is then passed, and the electrodes moved if necessary to produce the requisite resistance. In about ten minutes, the copper having melted between the electrodes, the distance between them is increased while the current is raised to 1,300 amperes of fifty volts E.M.F. As the resistance is increased the temperature rises, the alumina is reduced to the metallic condition and alloys with the copper, while its oxygen forms carbon monoxide and burns at the openings in the cover with a white flame. After about five hours the operation is completed. The alloy produced is brittle, consisting of copper and 15 p.c. or upwards of aluminium. When boron or silicon oxides have been added, the bronzes produced contain these elements. It is melted, cast into ingots, the percentage of aluminium determined, and sufficient copper added to produce 'aluminium bronze,' or the required alloy.

When other metals, such as iron, nickel, silver, &c. are substituted for copper, corresponding alloys are produced.

The slag produced is hard and compact, but soon falls to a fine alkaline powder; it contains alumina, calcium aluminate, with traces of copper, silicon, &c.

Pure aluminium cannot be produced satisfactorily by this method, as it remains, to a great extent, mingled with the carbon.

See further, W. P. Thompson (S. C. I. 1886, 206); Mabery (Am. S. 308), and (Am. 1887, 11).

An electric furnace for the reduction of cryolite has been invented by Kleiner (Eng. Pat. 1886, 8,531).



The following analyses, taken from Hoffmann's *Ber. Entwick. Chem. Ind.* (1) 603, show the composition of commercial aluminium:—

	1	2	3	4	5	6	7	8	9	10
Locality . . . .	Paris	Paris	Berlin	Paris	Paris	Paris	Bonn	Nanterre (Morin)		
Analyst . . . .	Salvetat	Salvetat	Mallet	—	Dumas	Dumas	Kraut	Kraut	Kraut	Sauerwein
Aluminium . .	88.35	92.97	96.25	92.60	92.5	96.16	94.7	—	—	97.2
Silicon . . .	2.87	2.15	0.45	0.45	0.7	0.47	3.7	0.04	0.12	0.25
Iron . . . .	2.40	4.83	3.29	7.55	6.8	3.37	1.6	1.62	2.26	2.40
Copper . . .	6.38	—	—	—	—	—	—	—	—	—
Lead . . . .	trace	—	—	—	—	—	—	—	—	trace
Sodium . . .	—	trace	trace	—	—	—	—	—	—	—

Absolutely pure aluminium may be prepared by the method adopted by Mallet in his determination of the atomic weight of that element (*Tr.* 171, 1,018; *C. N.* 46, 178). Ordinary commercial aluminium is converted into bromide by the direct action of bromine. On account of the violence of the action the metal should be immersed only for a short time, at intervals, until dissolved, or should be added in very small pieces. The bromide so produced is freed from bromine by distillation and fractionally distilled, that portion boiling uniformly at 263.5°C. being reserved. This portion is colourless, entirely soluble in water, and consists of the pure bromide.

It is heated with sodium (which has been carefully freed from oil and well scraped) in a crucible made of a mixture of pure alumina and sodium aluminate. The amount of sodium used should not be sufficient to reduce the whole of the bromide, or the aluminium is liable to contain sodium. The globules of metal are fused together before the blowpipe on a bed of alumina, immersed for a short time in hydrochloric acid, washed and dried. Pure aluminium might also be produced by the electrolysis of the pure bromide or chloride.

*Purification.*—On account of the low specific gravity of aluminium there is a considerable tendency for portions of the slag to remain in the metal. The presence, especially, of aluminium chloride is very injurious, and such metal, though quite pure in appearance, soon becomes attacked in spots on exposure to the atmosphere, and coated with alumina. According to Morin, the metal should be melted in a plumbago crucible and exposed to the air at a red heat. Acid fumes are evolved from the decomposition of the chloride, &c., and a white seum collects on the surface. The crucible is taken from the furnace and the seum removed by a cast-iron rod. This operation must be repeated three or four times before the whole of the slag is removed.

The purification from metallic impurities is extremely difficult. The only method of obtaining satisfactory metal is to produce it in a state of purity in the first instance by using only pure materials.

No process of removing *silicon* is known. When heated in fused soda the superficial silicon is removed. Metal so treated takes a good polish.

*Iron* may be partially removed by a process of lixivation, and iron or *copper*, by fusion with

potassium polysulphide, chlorate, and nitrate, but the separation is very incomplete.

*Zinc* may be driven off as oxide by exposure of the molten metal to the air. The complete separation only takes place at an extremely high temperature.

*Lead* is removed by cupellation. Peligot recommended cupellation of impure aluminium with lead for the removal of other impurities; according to Deville the metal may be much improved by that method.

Devil recommends the following as the best general method of purification. A cast-iron crucible is thoroughly oxidised on the surface by a little fused nitre and the metal placed therein, covered with a layer of potassium nitrate and heated to redness. The iron, copper, &c., are thus oxidised and pass away in the slag. If the temperature be too high the aluminium itself rapidly acts upon the nitre with formation of potassium aluminate.

(For the influence of small quantities of impurity *v. Alloys, infra.*)

*Physical Properties.*—Commercial aluminium is a white metal with a bluish tinge, which becomes intensified when the metal is worked, and when much silicon and iron are present. It has been obtained in crystals resembling octahedra; *pure* aluminium is not magnetic. The specific gravity of the cast metal is about 2.56; this may be increased to 2.688 by rolling. Its specific heat is about 0.218.

It melts at 600°C. (Pictet); about 700° (Castner, *com.*), and appears to be quite non-volatile.

Notwithstanding its low melting-point it is difficult to liquefy the metal on account of its high specific heat; its latent heat also appears to be considerable. It should be fused in an open vessel without a flux.

Aluminium contracts on solidifying. The largest casting of this metal is said to be the cap of the Washington Monument, weighing 8½ lbs. (*Min. Res. United States, 1883-1884*).

Taking the electric conductivity of silver at 0°C. as 100, that of aluminium at 0°C. is 34.0 (Matthiessen). The conductivity for heat of silver being 100 at 19.6°C., that of aluminium is 33.7. Slightly different conductivities from the above are given by Lorenz (*A. Ch.* 2, 13, 422 and 582).

Aluminium is extremely malleable, especially when pure, and may be beaten into leaf like gold and silver. Its temper, however, is quickly lost and the metal requires frequent

annealing, especially as it becomes thinner. The leaf is said to form a good and durable substitute for silver. It may be drawn into fine wire if frequently annealed at a low heat. The best temperature for working is said to be 100° to 150°C. In elasticity and hardness it is about equal to silver. The hardness increases when hammered and diminishes after heating.

W. H. Barlow (Brit. Assoc. Rep. 1882, 668) has determined the more important mechanical properties of a bar of aluminium  $\frac{1}{4}$  inch square and 3 feet long. Its sp. gr. was 2.688; its modulus of elasticity 10,000; its range of elasticity high, a bar stretched  $\frac{1}{200}$  of its length before breaking. Its tensile strength was 26,800 lbs. (about 12 tons) per square inch. The length of a bar able to support its own weight was 23,040 feet, i.e. equal to that of ordinary steel and more than double that of bronze. Kamarsch (D. P. J. 172, 55) finds, for a wire 0.225 mm. in diameter a tensile strength of 12.975 kilos per square mm., and for a wire 0.145 mm. in diameter, a tenacity 11.845. According to Mallet (C. N. 46, 178), absolutely pure aluminium is as white as tin, but of greater lustre, with no bluish tinge, softer and more malleable, and apparently less fusible than the ordinary metal. Its hardness is less increased by hammering. Its sp. gr. is  $2.583 \frac{40}{100}$  and its sp. heat between 0° and 100°C. is 0.2253; higher than that of any other metal except lithium and glucinum, as might be expected from its low atomic weight. Considerable difficulty is experienced in soldering aluminium. Mourey (D. P. J. 166, 205) recommends several solders; a generally useful one contains aluminium 6, copper 4, zinc (free from iron) 90; or for heavier work, aluminium 12, copper 8, zinc 80; the latter is also recommended by Van der Weyde.

For burnishing and engraving aluminium, the ordinary media are unsuitable. According to Mourey and others an emulsion of equal parts of rum and olive oil is most satisfactory. The appearance of the manufactured articles is improved by a frosted appearance. This is produced by plunging the article momentarily into a weak solution of caustic alkali, washing well and immersing in dilute nitric acid. Aluminium is extremely sonorous, especially when pure. If suspended by a fine wire, a bar when struck emits a clear, sweet, and prolonged sound. Lissajous has prepared tuning-forks of this metal, the action of which was very satisfactory. Dumas (C. R. 90, 1,027, and J. Ph. 2, 12) has shown that ordinary aluminium contains nearly its own bulk of hydrogen and a small quantity of carbon dioxide. The whole of this gas is evolved, somewhat suddenly, at a white heat, about the melting-point of porcelain. The pure metal prepared by Mallet only evolved about  $\frac{1}{3}$  of this amount (C. N. 42, 285). It appears, therefore, that the quantity of gas absorbed depends on the method of preparation. The presence of this gas would not appreciably affect Mallet's determination of the atomic weight of aluminium from the metal.

*Chemical Properties.*—When heated in air, especially at a white heat, aluminium is oxidised. The presence of silicon increases the action, and when this is present in considerable

quantity, the alloy burns brilliantly, forming a silicate of aluminium. In foil, however, the metal burns readily in air or oxygen.

Commercial aluminium is rapidly oxidised by water or steam at high temperatures. Aluminium leaf slowly decomposes in water at 100° C., becoming finally converted into the translucent hydrate which retains the form of the metal.

According to Hinze (D. P. J. 227, 277) aluminium, when pressed against moist platinum, becomes covered with alumina, from galvanic action on the water.

At a red heat sulphur converts aluminium into the sulphide; the foil burns in sulphur vapour. Sulphuretted hydrogen, ammonium sulphide, &c., are without action upon it. Aluminium combines with phosphorus but not with hydrogen. It combines with carbon, and the carbon appears to exist in the metal as a carbide, as in iron and steel. It is rapidly attacked by the halogens with considerable rise of temperature.

Dilute sulphuric acid has no action, even in presence of other metals (De la Rive). When much silicon is present, silicon hydride is evolved and the metal slowly dissolves. The cold concentrated acid has a slight action; when heated, the metal is rapidly dissolved with evolution of sulphurous anhydride. Cold concentrated or dilute nitric acid is without action; even on heating solution is slow, and again ceases on cooling. On this account Hulot has proposed the substitution of aluminium for platinum in Grove's battery.

Pure aluminium is attacked by hydrochloric acid. The commercial metal dissolves readily in dilute or concentrated acid, both hot and cold, more rapidly in strong acid or when the metal is very impure. At a very low temperature gaseous hydrochloric acid converts the metal into the chloride. Corresponding effects are produced by aqueous and gaseous hydrobromic, hydriodic, and hydrofluoric acids.

The action of organic acids on aluminium is almost inappreciable. In presence, however, of sodium chloride these acids have a slight solvent action. Under like circumstances, tin and copper would be much more affected, with the production of injurious salts, while the salts of aluminium are quite harmless and are almost entirely precipitated and rendered insoluble on boiling.

Perspiration, being acid, has no apparent effect; saliva, on account of its slight alkalinity, acts very slowly. Aluminium tubes have been used for insertion in the human body where much purulent matter was present, without perceptible corrosion.

Aluminium when fused with potash or soda is unaffected even at a dull red heat, but the superficial silicon is removed; metal so treated takes a good 'mat.'

Solutions of caustic alkalis act with considerable energy, with formation of an aluminate. Calcium hydrate has a less rapid action.

Dry ammonia gas has no action; solution of ammonia slowly converts the metal into hydrate, and a portion passes into solution.

Pure aluminium is less acted upon by most reagents than the commercial metal (Mallet).

*Action on metallic solutions.*—Aluminium, especially in the form of foil, has a considerable action on many salts in solution. The action of sulphates and nitrates is usually very slow. All chlorides, except those of the alkalis and alkaline earths, are readily decomposed, even *aluminium chloride* solution dissolves the metal with evolution of hydrogen. Bromides and iodides have corresponding effects. The presence of sodium or other chloride in solutions of other salts much facilitates their action.

From a neutral or feebly acid solution of silver nitrate, silver is precipitated slowly; from an ammoniacal solution of the chloride, silver is rapidly precipitated as a crystalline powder.

From the nitrate or sulphate of copper, precipitation is slow, from the acetate quicker, and from the chloride or other salt in presence of sodium chloride, rapid and complete.

Mercurous salts are decomposed with formation of an amalgam. Lead and zinc are readily precipitated (*v. also* Cossa, Z. [2] 6, 380 and 413).

*Action on dry salts and oxides.*—The action of aluminium, when heated with certain salts and oxides, is peculiar, and shows, especially at high temperatures, the tendency of this metal to form aluminates.

It is not affected by potassium nitrate except above a red heat; it is then rapidly oxidised with formation of potassium aluminate. With alkaline carbonates combination takes place at a red heat with separation of carbon, and with alkaline sulphate combination takes place suddenly at redness with explosive violence; in both cases aluminates are formed.

When finely divided aluminium is mixed with oxide of copper, lead, or iron, combination takes place at a *white* heat only, with such violence as frequently to shatter the crucible. In the case of lead and copper oxides, aluminates are produced, and with iron an alloy of iron and aluminium (Tissier).

When heated with silicates or borates, aluminium liberates silicon or boron, forming an aluminate with the base. Fused silver chloride is reduced to metal; zinc is reduced from its fused chloride, whilst magnesium chloride is not affected (Flavitzky, B. 6, 195). The vapour of mercuric chloride is reduced with such energy by heated aluminium that the metal fuses.

*Detection.*—Compounds of aluminium, when heated, moistened with solution of cobalt nitrate, and again strongly ignited, produce a fine sky-blue colour (*Thenard's blue*, *q. v.*, art. COBALT).

Aluminium compounds are usually colourless. Silicates and other compounds insoluble in acids require to be finely powdered, mixed with 4 parts of sodium carbonate or fusion mixture, and ignited strongly in a platinum crucible. The aluminium having thus become converted into sodium aluminate, is dissolved out with hydrochloric acid, evaporated to dryness to render any dissolved silica insoluble, and treated with dilute hydrochloric acid. The aluminium is then present as chloride.

Aluminous solutions, on addition of an alkali, give a white gelatinous precipitate of hydrate, soluble in excess of the precipitant and in acids. Ammonia produces the same precipitate, which is only slightly soluble in excess, and is entirely

reprecipitated on boiling off the excess of ammonia.

*Estimation.*—Aluminium is always precipitated as the hydrated oxide  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ .

For this purpose the solution, which, in presence of alkalis or alkaline earths, is mixed with excess of ammonium chloride, is treated with a *slight* excess of ammonia, and the solution boiled until the free ammonia is expelled. The hydrate, having thus become totally precipitated, is filtered, well washed, dried and ignited in a platinum crucible, the heat being finally raised to bright redness for five minutes over the blowpipe. The weighed residue consists of anhydrous oxide,  $\text{Al}_2\text{O}_3$ , and contains 53.39 p.c. of aluminium. The separation from other metals is not difficult. The heavy metals may be precipitated from the *acid* solution by sulphuretted hydrogen, leaving the aluminium in solution, whilst the precipitation in presence of ammonium chloride in excess separates it from the alkalis and alkaline earths. From chromium and iron the separation is less simple. Chromium may be separated as follows:—The precipitated oxides are dried, mixed with 2 parts potassium nitrate and 4 sodium carbonate in a platinum crucible and fused. Alkaline chromate and aluminate are thus produced. The mass is digested with water and a small quantity of potassium chlorate and hydrochloric acid are then added, and the solution is evaporated to a syrup, with occasional addition of potassium chlorate to destroy the excess of hydrochloric acid and prevent its reducing action on the chromate. The aluminium in the diluted solution is precipitated as above by ammonia, leaving the chromate in solution.

For the separation from iron, the precipitated hydrated oxides are dissolved in the minimum quantity of hydrochloric acid and treated with an excess of *pure* strong potassium hydrate solution, boiled for a few minutes, diluted, filtered and well washed. The ferric oxide is thus precipitated and separated from the soluble alumina. The solution and washings are acidulated with hydrochloric acid and precipitated by ammonia. On account of its solvent action upon glass, the treatment with potash should be performed in a porcelain dish, which is much less attacked, or, preferably, in one of silver.

*Alloys.* Aluminium unites easily with most metals, usually with evolution of heat. The alloys are frequently brittle when either constituent is in excess. Many of them are easily worked and possess special properties, such as resistance to corrosion, hardness, fine quality of colour, great tenacity, &c.

The malleability of aluminium is not much impaired by the addition of gold, silver, or tin, but the presence of iron, and especially of silicon, is very injurious.

With *silicon* aluminium unites in almost all proportions, either directly or by its action on silicious materials; for this reason the fusion or preparation of this metal should not be performed in any silicious crucible in presence of a flux. The presence of silicon renders aluminium brittle and much less permanent. The alloy containing 10 p.c. silicon is grey and brittle. Wöhler has prepared an alloy containing 70 p.c. silicon, which still appeared metallic.



With iron the alloys are of especial interest. The presence of a small quantity of iron is very injurious; it renders the aluminium crystalline, and raises the melting-point. The alloy containing 5 p.c. of iron is hard and brittle; with 8 p.c., the alloy crystallises in needles and on heating separates into a more liquid alloy containing but little iron and a skeleton very rich in that metal. Michel (A. 115, 102) has prepared an alloy which crystallises in six-sided prisms, corresponding to AlFe.

The valuable properties imparted to iron and steel by the presence of a small quantity of aluminium have long been known; Faraday (Quarterly Journ. Roy. Inst. 1819, 290) found from 0.013 to 0.069 p.c. of aluminium in certain samples of Bombay wootz, though it has been shown by Henry and others that this metal is not always present. About the same time S. B. Rogers showed the presence of aluminium in some of the best quality of pig-iron made in South Wales, and found that a steel to which 0.8 p.c. of aluminium had been added in the form of an alloy with iron, was rendered harder and stronger and resembled the best wootz (Rogers, Metallurgy, 1858, 14). A superior steel was prepared by Sir Charles Knowles, which was stated to owe its value to the use of *kaolin* and consequent introduction of aluminium into the metal in its preparation (Mining Journal, 1859, 118).

Messrs. Cowles Bros. have exhibited a Siemens-Martini basic steel containing 0.2 p.c. aluminium, which welds with iron and shows no mark at the junction.

The addition of aluminium to iron or steel for the production of 'mitis castings' has been patented by P. Ostberg (Engineering, 1836, 360). Iron and steel, especially at temperatures far above the melting-point, absorb considerable quantities of gas, which impairs the value of the castings. It is stated that the addition of 0.05 or 0.1 p.c. of aluminium in the form of an alloy of iron containing 7 or 8 p.c. of aluminium to the fused iron or steel lowers the melting-point by 300° to 500° F., prevents the absorption of gas, and considerably increases the fluidity. The metal can then be easily cast. Small castings only have at present been produced; they are stated to resemble wrought iron, to be free from flaws, to require no annealing, and to have gained 30 to 50 p.c. of additional tenacity.

With copper, aluminium unites in all proportions. The presence of a small quantity of copper increases the hardness; with 3 p.c. copper the metal is whiter than aluminium and more easily worked; with 5 p.c. the alloy is about as hard as standard silver. The alloy containing from 30 to 40 p.c. copper is brittle, very hard, and crystalline; a further addition of that metal again reduces the hardness. With 30 p.c. of aluminium the alloy is hard and unworkable; that containing 20 p.c. is yellowish-white, and may be pulverised in a mortar. Alloys containing 10 p.c. or less of aluminium are all valuable, being hard, tenacious, and easily worked. The 7 p.c. alloy is the colour of 'green gold'; that containing 5 p.c. is more easily tarnished; the presence of even 1 p.c. of aluminium renders copper harder, more fusible, and more easily worked. Messrs. Bell Bros. give the sp.gr. of

these alloys as 3 p.c. aluminium, 8.691; 4 p.c., 8.621; 5 p.c., 8.369; 10 p.c., 7.689.

**Aluminium bronze.** Of these alloys the most important is that containing 10 p.c. aluminium, known as 'aluminium bronze.' It corresponds to the compound AlCu<sub>9</sub>, and was first prepared by Percy. It appears to be a true compound, for on the addition of a bar of aluminium to copper, fused in a plumbago crucible, combination at once commences, and the temperature rises to whiteness.

For the production of the best bronze both the aluminium and copper should be of the greatest possible purity. The impurities present in commercial copper lower the value of the alloy considerably. When first prepared it is very brittle, but becomes malleable after being fused two or three times.

Aluminium bronze is of a bright golden colour, of sp.gr. 7.689, *i.e.* about that of wrought iron; it takes a fine polish, and casts well. It is less acted upon by sulphurous gases and by vegetable acids and ordinary reagents than other alloys of copper (*v.* Proctor, C. N. 4, 5). It is malleable at all temperatures, but requires frequent annealing if worked when cold. The tensile strength of the best hammered aluminium bronze is equal to that of good steel; indeed, it is stated by many to surpass steel in that respect. According to Anderson its tenacity is about 96,000 lbs. per square inch, whilst that of the best gun-metal is 35,000 lbs., steel varying from 67,000 to 114,000 lbs. It has great power of resisting pressure, standing midway between the best steel and iron. Under a pressure of 59 tons per square inch it became distorted, but showed no sign of fissure. Its rigidity is 3 times that of gun-metal, 44 times that of brass; it is slightly less affected by change of temperature than those metals (Strange, P. M. 24, 508).

On account of its valuable properties, its lightness and beauty, aluminium bronze may be applied to an immense variety of purposes, its universal application being only retarded by its present high price. It is excellent for forging, casting, making tubes, &c. For the journals of machines it is superior to gunmetal; for physical and other delicate apparatus it is unsurpassed, both from its low sp.gr. and its resistance to corrosion.

The addition of nickel, zinc, bismuth, tin, &c., to this metal produces bronzes useful for special purposes. *Hercules metal*, containing copper, nickel, and a little aluminium; *argentan*, and *minargent*, are alloys of this type. With a certain proportion of silicon the tenacity of aluminium is said to be increased.

A corresponding improvement is effected by the addition of aluminium to brass. An alloy containing aluminium 2.5 p.c., copper 70 p.c., and zinc 27.5 p.c., is said to show nearly double the tenacity and considerably more than double the elongation of ordinary cast brass.

The presence of tin in aluminium renders it more fusible and brittle. According to Bourbouze (C. R. 102, 1,317) an alloy of aluminium 100, and tin 10 is strong, easily worked, may be soldered as easily as brass, is whiter and less affected by reagents than aluminium, and is very suitable for parts of optical instruments. Its sp.gr. is 2.85. The addition of alu-

minium to tin increases its hardness and tenacity. The alloys containing 5, 7, and 9 p.c. of aluminium are all easily worked and soldered. A larger proportion of aluminium is liable to separate out on melting.

The presence of *zinc* in aluminium renders it brittle and more fusible. The alloy containing 3 p.c. of zinc is brilliant in appearance and harder than aluminium. With 25 p.c. of aluminium the grain is fine and even; with 30 p.c. of that metal the alloy is crystalline and brittle.

Aluminium combines in all proportions with *cadmium*, forming malleable fusible alloys.

Small quantities of *silver* increase the hardness and elasticity and lower the melting-point without rendering aluminium brittle. The alloy containing 4 p.c. silver has been used for the beams of delicate chemical balances. When the addition exceeds 5 or 6 p.c. the metal becomes brittle; the 50 p.c. alloy is as hard as bronze, but very brittle. '*Tiers argent*' consists of 1 part silver and 2 parts aluminium; it is of considerable hardness, and is used for table-spoons &c. The addition of 5 p.c. of aluminium to silver renders it as hard as standard silver and very permanent.

The presence of aluminium in *gold* considerably alters its properties. The addition of 0.186 p.c. of aluminium to *pure gold* increases the tensile strength from 7 tons to 8.87 tons per square inch, a greater increase than is produced by the same amount of any other metal (Roberts-Austen, Roy. Soc. Rep. April 1888; C. N. 1888, v. 57, p. 133). With 1 p.c. aluminium the gold has the colour of 'green gold,' is hard but easy to work; with 5 p.c. aluminium it is white and extremely brittle, and with 10 p.c. white, brittle, and crystalline. Aluminium containing 10 p.c. of gold is white and hard.

*Nickel* and aluminium combine with incandescence when heated together. The presence of under 3 p.c. of nickel lowers the melting-point and increases the hardness and elasticity. Further addition renders the metal brittle.

Pure aluminium combines with mercury although not readily when the metals are heated together in an inert gas such as carbonic anhydride. The two metals combine rapidly in presence of alkalis. The amalgam may also be produced by electrolysis of mercuric nitrate, using a negative plate of aluminium, dipping in mercury. When aluminium is rubbed with wash leather impregnated with mercury, combination occurs; the surface rapidly oxidises, and becomes heated, with formation of concretions of alumina (Jehn and Hinze, B. 7, 1, 498). The amalgam oxidises rapidly, especially in moist air or in water, with formation of white alumina and separation of mercury. According to Hinze (D. P. J. 227, 277) this oxidation does not take place in *dry air*, and is due to a galvanic action on the water.

Alloys of *bismuth* with aluminium are hard and brittle. With *antimony* and *lead* aluminium does not unite, although traces of lead are frequently present in commercial aluminium.

*Sodium* unites readily with aluminium. The last traces of sodium are difficult to remove, especially, it is said, when the metal has been reduced from cryolite. The alloys are easily attacked by moisture, and burn in the air, with

oxidation both of the aluminium and sodium; that containing 2 p.c. of sodium decomposes water with ease. The necessity of thoroughly removing the whole of the sodium in the purification of aluminium is therefore obvious.

Aluminium also unites with *manganese*; with *platinum* it unites easily, forming fusible alloys. With *boron* aluminium unites in varying proportions. The so-called 'adamantine' and 'graphitic' boron appear to be borides of aluminium (Hampe, A. 1876, 75; and Deville and Wohler, *ibid.* 1867, 268), v. BORON.

Mallet (C. J. 1876, ii. 350) has prepared a nitride of aluminium in small crystals hard enough to scratch glass.

For further information respecting aluminium and its alloys, v. St. Claire Deville, L'Aluminium, Paris, 1859; and Reports on the Paris Exhibition, 1862, vol. i. 104-111; C. and A. Tissier, L'Aluminium, Paris, 1874; Mierzinski, Die Fabrikation des Aluminiums, Berlin, 1885; J. W. Richards, Aluminium and its Alloys, London, 1887.

#### Aluminium oxide Alumina $Al_2O_3$ .

Aluminium forms only one oxide,  $Al_2O_3$ , corresponding to and isomorphous with the sesquioxides of iron and chromium.

This oxide occurs native, colourless as *hyaline*, *corundum*, or coloured by metallic oxides, as *ruby*, *sapphire*, *oriental topaz*, &c. (*q.v.*). Very impure, dark, and usually associated with magnetite and *hamatite*, it occurs in large boulders in many districts and is used as a grinding and polishing material in the form of *emery* (*q.v.*). The native oxide crystallises in the rhombohedral system; in hardness it comes next to the diamond. The finely-coloured specimens are used as gems. It occurs almost pure in considerable quantities in the Alleghanies in Northern Georgia.

It may be prepared by the ignition of aluminium foil in air or oxygen; the oxide so produced is fused and as hard as corundum.

Amorphous alumina may be produced by ignition of the precipitated hydrate, pure aluminium sulphate or ammonia alum: in either case alumina alone is left.

It is white and soft, but becomes hard on strong ignition. According to H. Rose (P. A. 71, 430) the sp.gr. of the oxide after heating over a spirit lamp is 3.725; its density may be raised to 4, just about that of corundum, by ignition in a porcelain furnace, but it still remains amorphous.

When alumina is ignited with a salt of cobalt a fine blue colour is produced which is used as a pigment (*v. Thenard's blue*, art. COBALT).

When heated by the oxyhydrogen blow-pipe, alumina melts and crystallises, the addition of chromium oxide or a chromate imparts a ruby colour to the crystals.

Freny and Verneuil (C. R. 1888, 566) have prepared fine artificial rubies by heating to redness a mixture of barium fluoride and alumina containing a trace of potassium bichromate. The heat requires careful management. Fine rubies are thus formed in a friable matrix which may be separated by agitation with water. By former methods the matrix was hard and difficult to remove (Freny and Feil, C. R. 1877, 1,029, and 1887, 737). The crystals contain no barium,

easily scratch the topaz and possess the form and properties of natural rubies; their crystalline form has been determined by Descloiseaux (C. R. 1888, 567). By the addition of a little cobalt oxide before the fusion, sapphires may be produced.

Alumina is soluble, on strong ignition, in boric oxide; the latter may be driven off at an elevated temperature leaving crystalline alumina. By the addition of the proper oxides the corresponding aluminates may be produced, such as spinel (magnesium aluminate), and others, colourless or coloured by oxide of cobalt (blue), of chromium (red), and of iron (black) (Ebelmen, A. Ch. 3, 22, 211 and 33, p. 34).

Alumina is not affected by heat; nor by chlorine, except in presence of carbon. In any form it is converted into sodium aluminate by ignition with caustic soda and into sulphate by fusion with potassium bisulphate.

**Hydrated oxides.** Alumina occurs in three states of hydration, the mono-, di-, and tri-hydrates. The hydrate occurs, usually with corundum, as *diaspore*  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and in the important mineral *bauxite*. Alum-clay may also be included among the hydrates; it contains aluminium silicate in addition.

**Bauxite** occurs at Beaux in France, at Feistritz in Austria, and in a clay-like form at Wochein in Styria, known as *Wocheinite*. Its most important locality is Irish Hill near Larne in Co. Antrim, Ireland, where it occurs with lignite in the iron measures. It is found in three layers, the first from four to seven feet thick, the second of about equal thickness beneath a layer of basalt, and the third about forty feet thick containing much iron.

Bauxite always contains ferric oxide, but the finest or 'Gertrude' quality from Irish Hill is nearly as free from iron as good china clay. Bauxite is very largely used for the preparation of aluminium sulphate and of sodium aluminate. The varieties used for the preparation of aluminium are known as 'aluminium ore.' It is also used, mixed with fire-clay, dolomite or magnesite, as a fire-resisting material. With clay, sodium silicate, &c., it forms a valuable lining for furnaces such as Siemens's rotary furnace. When heated, it becomes extremely hard and is used as artificial emery. The following analyses show the composition of bauxite from Beaux, Wochein, Feistritz, and co. Antrim, Ireland:—

Locality . . . . .	Beaux		Wochein		Feistritz			Irish	
Analyst . . . . .	Deville		Drechs'er		Schnitzer			Siemens	
			Dark coloured	Light coloured	Reddish brown	Yellow	White	Raw	Calcined
$\text{Al}_2\text{O}_3$ . . . . .	60	75	63.16	72.87	44.4	54.1	64.6	35.0	44.48
$\text{Fe}_2\text{O}_3$ . . . . .	25	12	23.55	13.49	30.3	10.4	2.0	38.0	48.0
$\text{SiO}_2$ . . . . .	3	1	4.15	4.25	15.0	12.0	7.5	3.5	4.45
$\text{Na}_2\text{O} + \text{K}_2\text{O}$ . . . . .	—	—	0.79	0.78	—	—	—	—	—
$\text{H}_2\text{O}$ . . . . .	12	12	8.34	8.50	9.7	21.9	24.7	21.5	—
$\text{TiO}_2$ . . . . .	—	—	trace	trace	—	—	—	2.0	2.54

The following analyses by Leop. Mayer and O. Wagner (D. P. J. 248, 213) show that the appearance of bauxite cannot be relied on as a criterion of its value. The origin of the samples is not given.

	Appearance	Hygroscopic moisture	Combined water	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{SiO}_2$	$\text{MnO}_2$	CaO	MgO	$\text{P}_2\text{O}_5$
1	Pure white . .	2.33	13.86	29.80	3.67	44.76	—	2.75	0.84	1.47
2	Yellow . . . .	1.03	27.85	43.22	14.39	10.43	—	1.61	—	1.13
3	" . . . . .	1.30	27.70	50.38	11.68	8.34	trace	trace	trace	0.61
4	Red . . . . .	1.34	23.12	33.86	25.69	12.41	2.42	trace	—	0.53
5	" . . . . .	1.31	23.81	46.18	22.05	4.82	—	0.89	—	0.66
6	" . . . . .	0.95	20.83	62.10	6.11	5.06	2.01	3.20	trace	trace
7	" . . . . .	1.17	4.75	21.80	3.75	60.10	—	6.06	2.49	trace

Other analyses of bauxite and of alum clay are given under *Aluminium sulphate*.

**Aluminium trihydrate**  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  or  $\text{Al}(\text{HO})_3$ . This compound is the ordinary hydrated oxide precipitated by the addition of an alkali to a solution containing an aluminium salt. In its preparation from insoluble minerals a solution of sodium aluminate is usually first produced, from which the oxide is then precipitated by carbon dioxide. Its preparation in this manner has already been described (pp. 64 *et seq.*). When freshly precipitated, it is a white gelatinous solid which loses a portion of its water at 100° C. and becomes soft and friable; this water is partially reabsorbed with formation of a stiff paste on addition of water. At a strong red heat it be-

comes anhydrous and contracts considerably. The hydrate is easily soluble in acids and in caustic alkali.

When boiled with water containing one drop of a 1 p.c. solution of alizarin, the hydrate assumes a bright-red colour, not removed by a weak solution of acetic acid. This test easily distinguishes it from gelatinous silica.

Aluminium hydrate possesses a powerful affinity for many organic substances, and combines with a large number of colouring matters, precipitating them entirely as *lakes*. On this property depends the use of alum mordants (red liquor, &c.). They precipitate the hydrate upon the fibre of the goods to be dyed, and this is the *mordant* or fixing agent which retains the colour.



**Sodium aluminate**  $\text{Al}_2\text{O}_3\cdot 3\text{Na}_2\text{O}$  or  $\text{Al}_2(\text{NaO})_6$ . This salt is now prepared on a large scale, both to be used as such and as an intermediate product in the preparation of the sulphate and other salts of aluminium.

Its formation depends upon the property possessed by alumina of acting as an acid in presence of a powerful base.

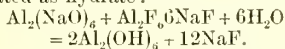
Its preparation from bauxite has been described on page 64. It may also be produced by passing a current of steam through a heated mixture of bauxite and common salt, and by the ignition of a mixture of bauxite, sodium sulphate, and carbon, but in the latter case its purification from the sodium sulphide simultaneously produced is difficult. It is also formed in the preparation of soda from *cryolite*. According to Thomsen's method, powdered *cryolite* is ignited at a red heat with chalk, forming sodium aluminate and calcium fluoride:—

$\text{Al}_2\text{F}_6\cdot 6\text{NaF} + 6\text{CaCO}_3 = \text{Al}_2(\text{NaO})_6 + 6\text{CaF}_2 + 6\text{CO}_2$ .  
The mass produced is lixiviated with water and filtered. From this aluminate the hydrate is precipitated by carbon dioxide with formation of sodium carbonate:—

$\text{Al}_2(\text{NaO})_6 + 3\text{CO}_2 + 3\text{H}_2\text{O} = \text{Al}_2(\text{OH})_6 + 3\text{Na}_2\text{CO}_3$ .  
The hydrate is usually made into aluminium sulphate by solution in sulphuric acid or it is converted into alum.

An entirely different process has been introduced by Sauerwein. The finely powdered *cryolite* is boiled with milk of lime forming aluminate as before:—

$\text{Al}_2\text{F}_6\cdot 6\text{NaF} + 6\text{CaO} = \text{Al}_2(\text{NaO})_6 + 6\text{CaF}_2$ .  
For the conversion of the aluminate into oxide Sauerwein applies a peculiar property possessed by that salt which shows the readiness with which alumina loses its acid properties and again becomes basic. Sodium aluminate, when mixed in equivalent proportions with any haloid salt of aluminium, is decomposed; the sodium combines with the halogen while the whole of the aluminium is precipitated as hydrate. On the large scale the haloid salt used is *cryolite*. The finely powdered mineral is stirred into the clear liquid from the previous operation, and the alumina precipitated as hydrate:—



Sodium aluminate is a white, infusible, amorphous solid, easily soluble in both cold and hot water. The concentrated solution rapidly deposits alumina, leaving in solution a basic aluminate, which on evaporation is obtained as a fusible and hygroscopic mass. The addition of any acid at once decomposes it with precipitation of alumina. This alumina is pure and free from alkali, which is never the case when alkaline precipitants have to be used. It may be used as a mordant in dyeing and calico printing, but an acid and not, as in the case of alum, an alkaline bath must be used. For the production of *lakes* the colouring matter is mixed with the aluminate solution and precipitated by the addition of sulphuric acid. According to Morin these lakes are richer than those obtained from alum and are produced at about one half the cost.

**Potassium aluminate**  $\text{Al}_2\text{O}_3\cdot 3\text{K}_2\text{O}$  or  $\text{Al}_2(\text{KO})_6$  is obtained in hard glistening crystals when alumina is fused with potash, the mass boiled in water and evaporated *in vacuo*.

**Aluminium chloride**  $\text{Al}_2\text{Cl}_6$ . This compound was first prepared in 1824 by Oersted, by passing chlorine over a mixture of alumina and charcoal heated to redness. The method and apparatus resemble that used in the preparation of the double chloride, omitting the sodium chloride.

According to P. Curie (C. N. 28, 307) it may be easily prepared as follows:—Anhydrous alumina, or, less satisfactorily, clay, is strongly heated in a tube and subjected to a current of hydrochloric acid impregnated with carbon bisulphide by bubbling through that liquid. Aluminium sulphide appears to be formed and at once decomposed by the hydrochloric acid yielding aluminium chloride and sulphuretted hydrogen. The condensed chloride may be freed from sulphur by distillation with iron filings.

A solution of the chloride may be obtained by dissolving the hydrate in hydrochloric acid.

The pure anhydrous chloride is a white, waxy, crystalline solid; in presence of a trace of iron it becomes yellowish. On heating it volatilises without fusion. If large pieces be quickly heated they fuse and boil at  $180^\circ$  to  $185^\circ\text{C}$ . (Liebig). It is very hygroscopic, and evolves hydrochloric acid on exposure to the air; easily soluble in water; soluble in alcohol and ether. When deposited from a solution in hydrochloric acid, it forms crystals of the formula  $\text{Al}_2\text{Cl}_6\cdot 12\text{H}_2\text{O}$ .

It absorbs ammonia and combines with many metallic chlorides, forming double chlorides, the most important being that with sodium. Aluminium chloride has been recommended by Filsinger (C. Z. 10, 1,270) for the preservation of wool, and by Saget (C. N. 45, 113) and others (S. C. I. 1882, 185 and 230) for the production of a discharge on indigo blue. An impure chloride containing calcium and sodium salts is stated to be largely used as a disinfectant under the name 'Chlor Alum.'

**Double chloride of aluminium and sodium**  $\text{Al}_2\text{Cl}_6\cdot 2\text{NaCl}$ . This compound may be produced by fusing together the proper proportions of aluminium and sodium chlorides. Its commercial preparation has been fully described on page 64. It is a colourless crystalline solid, melting at  $185^\circ\text{C}$ . (Deville) and volatilising at a red heat. It is slightly hygroscopic, but much less so than aluminium chloride; it is also more stable and more satisfactory in use than that substance, and gives up nearly the whole of its aluminium when reduced by sodium.

**Aluminium bromide**  $\text{Al}_2\text{Br}_6$  is most readily prepared by the action of bromine on metallic aluminium. The action is violent, and the metal should only be added gradually. A lump of aluminium weighing twenty grams became strongly heated and even fused on being placed in cold bromine (Mallet, T. 171, 1,018).

It may also be prepared by the action of bromine on a strongly heated mixture of alumina and carbon, and, in solution, by dissolving the hydrate in hydrobromic acid. It crystallises in colourless shining laminae, which melt at  $93^\circ\text{C}$ . (Deville and Troost) and boil at  $263\cdot 3^\circ\text{C}$ . (at 747 mm.) (Mallet).

Like the chloride, it forms a double bromide,  $\text{Al}_2\text{Br}_6\cdot 2\text{KBr}$ .

**Aluminium iodide**  $\text{Al}_2\text{I}_6$  may be prepared by heating aluminium with iodine in a closed tube.

It melts at about  $185^{\circ}$  (Weber) and boils at  $350^{\circ}\text{C}$ . (Deville and Troost); its vapour is combustible. It dissolves in water, alcohol, and carbon disulphide.

**Aluminium fluoride**  $\text{Al}_2\text{F}_6$ , may be prepared by the action of gaseous silicon fluoride, or of hydrofluoric acid upon aluminium. It forms transparent rhombohedra, volatile at a red heat, insoluble in water and unacted upon by acids. In solution in hydrofluoric acid, it appears to form the compound  $\text{Al}_2\text{F}_6 \cdot 6\text{HF}$ , corresponding to the double fluoride of aluminium and sodium.

**Cryolite**  $\text{Al}_2\text{F}_6 \cdot 6\text{NaF}$ . This important compound may be prepared artificially. It occurs in quantity only in one locality, in a large vein in the gneiss at Ivigtuk, in Greenland.

It is a semi-transparent, white, crystalline, brittle solid, which melts at the edges in a candle flame. Its hardness is 2.5 to 3; its sp.gr. 2.95. When impure it is frequently yellowish-red or even black.

Cryolite is used as a flux in the manufacture of aluminium; for making salts of sodium and aluminium; and formerly, for the manufacture of an opaque, porcelain-like glass. See further, Benzon (Hoffmann's Ber. Entw. Chem. Ind. [1], 660).

**Aluminium sulphide**  $\text{Al}_2\text{S}_3$ , may be prepared by the action of a strong heat on a mixture of aluminium and sulphur, or by heating alumina to bright redness in the vapour of carbon bisulphide. It forms a yellow, glassy mass, which fuses with difficulty, and burns in air with production of alumina and sulphur dioxide. It is at once decomposed by water.

**Aluminium sulphate**  $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 18\text{H}_2\text{O}$ , or  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ . Aluminium sulphate occurs naturally in considerable quantities. As *alunogen*, *halotrichite*, or *hair salt*, it is found as hydrated sulphate containing ferrous oxide in volcanic districts, at Bilin in Bohemia, Copiapo in Chili, &c. It also occurs in pyritic shale. A sample of *feather alum* from Friesdorf, Bonn, analysed by Rose, gave  $\text{SO}_3$  37.4 p.c.,  $\text{Al}_2\text{O}_3$  14.9 p.c.,  $\text{FeO}$  2.5 p.c.,  $\text{H}_2\text{O}$  45.2 p.c., with traces of K, Na, Mg, and  $\text{SiO}_2$ .

*Aluminite* has been found at Mühlhausen, Bohemia, of the composition  $\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 9\text{H}_2\text{O}$ .

It occurs in large quantities as a hydrated double sulphate of aluminium and potassium in *alum-stone*, *alunite* or *alum rock*, in seams in volcanic rocks, at Tolfa near Civita Vecchia; at Puy-de-Dôme; in hard masses in Hungary, and in many other localities. It usually occurs in fibrous compact masses in trachyte, of colour varying from white to red or brown, being produced by the action of sulphurous gases upon trachytic rocks rich in felspar.

The *alunite* from Tolfa contains from 32 p.c. to 17.5 p.c. alumina. According to Guyot (C. R. 95, 693) the average composition is:—Alumina 27.6, sulphuric acid 29.74, potash 7.55, water 11.20, iron 1.20, silica 22.70.

Large deposits of white and semitransparent alunite are said to occur in Gloucester, New South Wales, yielding alum perfectly free from iron on calcination and lixiviation (Emerson Mac-Ivor, C. N. 1888, 64).

Aluminium sulphate may be produced by solution of the hydrated oxide or silicate in

sulphuric acid. It is largely prepared from bauxite, alum clay, and china clay. Bauxite or alum clay are preferable to china clay, as they may be at once treated with acid, whereas china clay requires a preliminary calcination; the latter, however, contains less iron. When *china clay* is used, it is selected as free as possible from iron and grit, and is calcined in a reverberatory or muffle furnace. It is thus rendered porous and more easily soluble in acid whilst a portion of the iron present becomes insoluble. The temperature should be carefully regulated; if too high, the mass partially vitrifies, and is then almost insoluble in acids. The calcined mineral is finely ground and mixed in a lead-lined boiler with one-half its weight of sulphuric acid of 1.615 sp.gr.; sufficient water is added to reduce the density to 1.375 and the mixture is slightly heated. A rapid action soon ensues, and 75 p.c. of the alumina together with most of the iron is dissolved. The heating is continued until the acid is saturated, and the solid mass produced on cooling is cut into blocks and ground into coarse fragments for the market. It then contains the whole of the silica, iron, and other impurities in the clay, and is known as 'alum cake,' or 'aluminous cake.'

Beveridge gives the following analysis of aluminous cake. No. 1 was exceptionally free from iron:—

—	1	2	3
$\text{Al}_2\text{O}_3$	12.30	11.54	11.54
{ corresponding to			
$\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3$	41.07	38.53	38.53
$\text{Fe}_2\text{O}_3$	0.05	0.16	0.21
$\text{SO}_3$	29.55	28.00	28.38
$\text{CaO}$	0.10	0.12	0.15
Free $\text{SO}_3$	0.40	0.50	1.83
Insoluble	26.50	22.40	20.08

For preparation of commercially pure sulphate, water is added to the mixture before solidification, the insoluble particles are allowed to subside, and the solution is evaporated until a portion solidifies on cooling. The iron may be precipitated from the solution by one of the methods described later. The product usually contains a few per cents. of potash alum from the potash present in the clay.

The substitution of bauxite for China clay was proposed by Chatelier in 1858. It has now largely replaced that substance on account of its ready solubility, no preliminary calcination being necessary. Eglinton alum clay is also used to a large extent. Its solubility is about equal to that of bauxite.

The following analyses show the general composition of these three minerals. (For further analyses and description of bauxite see *Hydrated oxides*.)

The treatment of bauxite for the preparation of 'alumino-ferrie cake,' as patented by Messrs. P. and F. M. Spence (1875), is as follows:—The mineral is digested with dilute sulphuric acid with the aid of steam until the acid is neutralised; the insoluble matter allowed to subside, and the solution evaporated to 100° Tw. (1.5 sp.gr.), and run into shallow partitioned lead

Quality . .	Bauxite (Irish Hill Bauxite Company)				Alum clay (Eglington Chemical Company)			China clay
	'Gertrude' quality	1	2	3	1	2	—	—
Analyst . .	Pattinson				Pattinson		Fresenius	Unknown
Al <sub>2</sub> O <sub>3</sub> . . .	59.37	53.83	52.00	46.13	52.37	42.42	48.83	39.74
Fe <sub>2</sub> O <sub>3</sub> . . .	0.53	1.57	4.57	15.14	1.29	1.54	2.24	FeO 0.27
CaO . . . .	0.21	0.62	0.79	0.18	0.48	0.46	0.62	0.36
MgO . . . .	0.11	0.13	0.20	0.26	trace	trace	0.17	0.44
K <sub>2</sub> O + Na <sub>2</sub> O .	0.03	0.01	0.08	0.28	0.06	0.04	0.14	—
TiO <sub>2</sub> (titanic acid)	6.35	5.80	6.20	4.20	5.20	9.40	5.02	—
SO <sub>3</sub> . . . .	0.04	0.07	0.07	0.10	0.35	0.08	0.51	—
P <sub>2</sub> O <sub>5</sub> . . . .	trace	trace	trace	trace	none	none	CO <sub>2</sub> 0.28	—
SiO <sub>2</sub> . . . .	11.43	8.67	12.00	10.40	13.15	27.50	15.88	46.32
Organic matter .	—	—	—	—	trace	trace	—	—
Combined water .	21.87	29.27	24.00	23.39	27.13	18.53	26.35	12.67
Total . . .	100.0	99.97	99.91	100.68	100.03	99.97	100.04	99.80
Amount of Fe <sub>2</sub> O <sub>3</sub> present for 15 parts of alumina (Beveridge)	0.130	0.43	1.31	4.92	0.32	0.54	0.68	0.11

coolers. It there solidifies, and is removed in blocks 18 or 20 inches square, each weighing about 1 cwt. It is yellowish-green in colour, contains much alumina, and a small proportion of iron and free acid. It is used in the preparation of all but the finest papers, and in the precipitation of sewage, refuse liquids, and in the clarification and decolorisation of water supplies. The following analysis shows its general composition:—Al<sub>2</sub>O<sub>3</sub> 11.26 p.c. (corresponding to Al<sub>2</sub>O<sub>3</sub>.3SO<sub>3</sub> 47.61 p.c.) Fe<sub>2</sub>O<sub>3</sub> 0.28 p.c. FeO 0.32 p.c. SO<sub>3</sub> (combined) 35.36 p.c. SO<sub>3</sub> (free) 0.45 p.c. Insoluble 0.06.

For the preparation of aluminium sulphate as formerly<sup>1</sup> used by Messrs. Duncan and the Messrs. Newlands for the purification of sugar, the finely-powdered bauxite is well mixed with sufficient strong sulphuric acid in an apparatus resembling that used in the preparation of superphosphate of lime, and the fluid mixture run into a brick tank. A violent action soon ensues, and the mixture solidifies. No heating is required, and the operation only occupies a few minutes; the product, however, contains all the impurities in the mineral.

Crude aluminium sulphate is usually prepared from bauxite as follows:—67 cubic feet of cold sulphuric acid 1.615 gr. is poured into a large lead-lined vessel provided with a mechanical agitator, also covered with lead; the liquid is heated slightly by steam, and 1 ton of dried powdered bauxite is then added. The action soon commences, and the mass swells. After the whole has subsided, more mineral is added in charges of about 2 cwt. until an additional half ton has been added. Sufficient water is poured in to prevent solidification, and the mixture heated by steam. When the acid has become nearly neutralised the liquid is diluted to 40°Tw.

(1.2 sp.gr.) and run into settlers. The clear liquid, of density 1.185, is decanted off, and contains about 90 p.c. of the alumina present in the mineral, its usual composition being:—

Sp.gr. 1.181. (36.2 Tw.).

		Grammes per litre	
Al <sub>2</sub> O <sub>3</sub>	3SO <sub>3</sub> . . .	193.42	= 57.92 Al <sub>2</sub> O <sub>3</sub>
Fe <sub>2</sub> O <sub>3</sub> . . .		1.80	} = 1.791 Fe
FeSO <sub>4</sub> . . .		3.52	
Free H <sub>2</sub> SO <sub>4</sub> . . .		1.57	
CaSO <sub>4</sub> . . . .		2.69	
H <sub>2</sub> O . . . . .		977.13	

1180.13

The purification of this solution from iron is a matter of the utmost importance. Aluminium sulphate contains a much larger proportion of the active principle, *alumina*, than alum, and, when quite pure, is available for all the technical uses to which the latter is applied. The sulphates of potassium or ammonium are of value only in forming with the aluminium sulphate a compound which can be readily purified by crystallisation and thus obtained both free from iron and of constant composition.

Many processes have been proposed for the removal of iron. In the mechanical process of B. Newlands (Eng. Pat. 1880, 5,287), the crude solution of sulphate is evaporated to 67°Tw. (at 200°F.), and cooled for 24 hours in leaden tanks 3 feet deep. About 60 p.c. of the sulphate thus crystallises out. The liquid is drained off, and the residue pumped or forced into lead-lined filter presses, the plates of which are covered with thick felt, and separated by metal rings. Here it is subjected to a pressure of about 200 lbs. to the square inch. The hard cake so produced contains about 67 p.c. of the total aluminium sulphate, and 0.05 to 0.1 p.c. of iron. When 'Gertrude' bauxite

<sup>1</sup> The works are now closed owing to the operation of the foreign sugar bounties.



has been used, the iron may fall as low as 0.04 p.c. The mother liquor, evaporated and similarly treated, yields a second and third crop of crystals containing less alumina and more iron. The following shows the general degree of purity of each crop (Strype):—

Amount of Fe <sub>2</sub> O <sub>3</sub> pre- sent for 15.35 parts	Crude liquor	1st crop	2nd crop	3rd crop	Residual liquor
Al <sub>2</sub> O <sub>3</sub>	0.679	0.065	0.130	0.259	2.312

By dissolving these crops of crystals and treating as before, the proportion of iron may of course be much further reduced. The addition of a small quantity of hydrochloric acid to the magma is said to facilitate the purification.

A method for the removal of iron from the mineral *before* solution has been patented by Messrs. Chadwick and Kynaston. The raw powdered bauxite is mixed to a thick cream with water, and treated with 5 to 10 p.c. of oxalic acid and sufficient hydrochloric acid to prevent the precipitation of insoluble oxalates. The mass is occasionally stirred for 7 to 10 days, and washed by decantation until free from oxalic acid. A great portion of the iron and some aluminium are thus removed as oxalate. Bauxite so purified is said to produce a sulphate containing from 0.1 to 0.2 parts of iron to 16 parts of alumina. Condry, in 1877, proposed the reduction of the iron by reducing agents, or its conversion into sulphide by sulphuretted hydrogen or a sulphide, and the removal of the metal or sulphide by dilute acid. The proportion of iron may thus be reduced to one-third (Newlands). The only processes, however, used commercially depend on treatment after the mineral has been brought into solution.

The first chemical process proposed was that of Weismann, and consisted in precipitating the iron by means of potassium ferrocyanide. The precipitate, however, subsides very slowly, and contains much alumina; the liquid still retains a portion after long standing, and the product, on evaporation, is blue and unsaleable. Kynaston has found that the whole of the blue precipitate may be deposited by the addition of a salt of copper or of zinc, and by certain other salts. The composite process as used by him includes the deposition of the greater part of the iron as ferric arsenite, and is as follows:—

Forty-five cubic feet of ordinary sulphuric acid from the Glover tower (145°Tw.) is placed in a lead-lined iron tank and heated by means of steam. The density is reduced by dilution to 90° or 95°Tw., and 26 cwts. of bauxite is added. When the action has moderated, 5 cwts. of bauxite mixed with 95 lbs. of commercial arsenious oxide are stirred in, followed by a further addition of 3 cwts. of bauxite. In order to oxidise all the iron, a little sodium chlorate or a hypochlorite is then added together with 200 lbs. of chalk made into a thin cream with water, and the whole is well agitated. The acid being neutralised, the muddy liquor is run into one of a series of lead-lined tanks on a lower level, which it nearly fills. After standing for three or four days a sample is treated with the chalk mixture; if the yellow tint becomes

deepened, a further addition of chalk is made to the bulk of the solution; and this treatment is continued until no further change is perceptible. In twelve or fourteen days from the commencement the clear solution is drawn off into another series of tanks on a still lower level. In this manner a great part of the iron is precipitated as insoluble arsenite, and remains behind with the undecomposed bauxite, silica, &c., in the upper tanks. The liquid then contains about 100 grains of aluminium sulphate and 0.2 grains of ferrous oxide per cubic inch, and would at once yield a product containing 0.05 p.c. to 0.06 p.c. of iron. For its complete purification the proper proportion of calcium ferrocyanide is added whereby the remainder of the iron is converted into Prussian blue. The precipitation of this substance is, however, incomplete, and after twenty-four hours 7 or 8 lbs. of copper or zinc sulphate is added and the mixture well agitated. In three or four days, it is said, the whole of the iron is precipitated, leaving the solution, occasionally, slightly blue. The liquid is then drawn off, treated with calcium sulphide (a few pounds for each ton of aluminium sulphate in solution), and the whole heated by a steam-coil to the boiling point. The excess of arsenic and copper (or zinc) having thus been removed as sulphides, the clear liquid is decanted, evaporated to 106° or 108°Tw., and, while boiling, poured into leaden trays and solidified. The product contains 16 p.c. of alumina, and is as free from iron as alum itself. The cost of purification per ton of sulphate is said to be 3s. for the precipitation with arsenic and 6d. or 9d. for the removal of the excess of that substance, &c. Persoz proposed the precipitation of iron by the addition of gelatinous silica; the precipitation, however, is not complete.

According to Fahlberg and Semper (Eng. Pat. 1881, 5,579), both ferrous and ferric salts may be precipitated from aluminium sulphate by agitation in the cold for about thirty minutes with lead peroxide, ferrous salts being first oxidised and then precipitated. No lead passes into solution unless chlorides be present. The composition of the precipitate is not known, but the peroxide may be regenerated by digestion in cold nitric acid. P. & F. M. Spence (Eng. Pat. 1882, 3,835) use manganese peroxide for the same purpose. In presence of reducing agents such as ferrous salts, &c., manganese passes into solution, and requires to be reprecipitated by addition of chlorine or a hypochlorite.

The use of metatimonic acid and metastannic acid (Hood and Salamon) has also been proposed for the precipitation of iron. The iron is first oxidised by the addition of bleaching powder, and the liquid is neutralised with chalk and agitated with the precipitant. Both substances may be regenerated by digesting the precipitate with sulphuric acid.

Beveridge has published the annexed analyses of the purified aluminium sulphate.

For further information regarding these processes, see:—Beveridge (S. C. I. 1886, 16-22); B. E. R. Newlands (S. C. I. 1882, 124); Kynaston (C. N. 40, 191 and 202). A neutral aluminium sulphate is prepared, as patented by Laur, by boiling a solution of the ferruginous sulphate

—	Newlands' mechanical process		Pure salts			
	Extra quality	Ordinary quality	No. 1	No. 2 purified by a manganese method	No. 3 Kynastou's arsenic and ferrocyanide method	No. 4
Al <sub>2</sub> O <sub>3</sub> . . .	14.84	14.70	14.95	14.85	16.00	16.20
Fe <sub>2</sub> O <sub>3</sub> . . .	0.06	0.12	0.046	trace	nil	trace
SO <sub>3</sub> . . . .	35.00	34.00	36.09	34.94	38.00	38.00
Free H <sub>2</sub> SO <sub>4</sub> .	0.32	0.40	nil	0.29	nil	nil
CaO . . . .	0.11	0.11	0.17	0.14	0.16	0.14
H <sub>2</sub> O . . . .	49.42	49.95	48.72	49.60	45.50	45.40
	99.75	99.88	99.97	99.82	99.66	99.74

with zinc. The iron is thus reduced to ferrous sulphate, a corresponding amount of zinc passing into solution. Potassium ferrocyanide then no longer produces a dark-blue precipitate, although excess of iron be present, and the precipitate produced by the addition of ammonia contains so much zinc oxide that a sample precipitated in this way containing 12 p.c. may appear to contain 15 p.c. of alumina (Debray, S. C. 1. 1882, 188).

Karl Reuss (B. 17, 2,888) gives the density of solutions of pure aluminium sulphate as follows:—

Per-centage	Density at 15°C.	Per-centage	Density at 15°C.
1	1.017	14	1.1467
2	1.027	15	1.1574
3	1.037	16	1.1668
4	1.047	17	1.1770
5	1.0569	18	1.1876
6	1.0670	19	1.1971
7	1.0768	20	1.2074
8	1.0870	21	1.2168
9	1.0968	22	1.2274
10	1.1071	23	1.2375
11	1.1171	24	1.2473
12	1.1270	25	1.2572
13	1.1369		

Per-centage	Density at 25°C.	Density at 35°C.	Density at 45°C.
5	1.0503	1.0450	1.0356
10	1.1022	1.0960	1.0850
15	1.1522	1.1460	1.1346
20	1.2004	1.1929	1.1801
25	1.2483	1.2407	1.2295

Very pure aluminium sulphate is produced from cryolite and from bauxite by converting them into sodium aluminate, free from iron, precipitating the alumina with carbon dioxide, and dissolving it in sulphuric acid (*v. Sodium aluminate*). It may also be prepared from blast furnace slag. The finely powdered slag is converted into chloride by digestion in hydrochloric acid; the solution evaporated to dryness, heated to render silica insoluble, and the residue converted into sulphate by digestion in sulphuric acid. According to Lürmann (D. P. J. 194, 351), if the slag contains 25 p.c. Al<sub>2</sub>O<sub>3</sub>, 42 p.c. CaO,

and 31 p.c. SiO<sub>2</sub>, 100 kilos would require 333 kilos of hydrochloric acid (34 p.c.), and 58 kilos of sulphuric acid (150°B.), producing 180 kilos of aluminium sulphate.

Aluminium sulphate crystallises with difficulty in thin, six-sided, flexible, nacreous plates containing 18 molecules of water; soluble in twice their weight of cold water, almost insoluble in alcohol. According to Persoz it crystallises more readily in presence of alcohol.

When heated, the crystals melt in their water of crystallisation and swell up, leaving a white porous anhydrous sulphate which only dissolves slowly in water. At a red heat, sulphuric oxide is evolved leaving pure alumina. Aluminium sulphate has a strong affinity for other sulphates, such as that of potassium, combining with them and forming crystalline double sulphates or 'alums.' Most methods of preparing alums depend upon the addition of potassium or ammonium sulphate to a solution of this salt. According to Reuss (B. 17, 2,888) the addition of 1 p.c. of potassium sulphate to a solution containing 7 p.c. or upwards of aluminium sulphate, at once produces a precipitate of alum.

The general industrial uses of this salt are the same as those of potassium alum. It is largely used in paper-making and in the preparation of red liquor as a mordant. The coarser preparations are employed for the precipitation of sewage.

For the detection of free acid in aluminium sulphate, Miller (B. 1883, 1,992) recommends the use of methyl orange. Pure sulphate turns it orange, free acid turns it a further red. A dilute solution of Congo red becomes blue in presence of free acid, but is not affected by the pure salt.

For the estimation of free acid, a weighed quantity of the powder is digested with strong alcohol for twelve hours, filtered, washed several times with strong alcohol and the solution diluted and evaporated to a syrup. When all the alcohol has evaporated, absolute alcohol is added, which precipitates most of the sulphate, and the solution is filtered, diluted, and titrated with standard soda solution and phenol phthalein. For the estimation of small quantities of iron in this salt *v. ALUMS*. Several basic aluminium sulphates are known. According to Sievert, a yellow basic sulphate, soluble in water, exists; its colour is not due to the presence of iron. An insoluble form has been prepared by Persoz by heating alum with an

excess of sulphuric acid, evaporating off the greater part of the acid and washing the residue until it is free from potassium bisulphate. It forms a mealy powder which is converted into the normal sulphate by prolonged boiling with water.

**ALUMINIUM BRONZE** *v. Alloys*, art. ALUMINIUM.

**ALUMS.** A number of compounds are included under this term. They all possess the constitution  $M_2SO_4 \cdot R_2O_3 \cdot (SO_3)_x \cdot 24H_2O$ , where M is a monatomic element or radicle such as potassium, ammonium, sodium, &c., and  $R_2O_3$  is a sesquioxide such as that of aluminium, iron, chromium, or manganese. They all crystallise in the regular system with 24 molecules of water.

In the alums to be considered here the sesquioxide is alumina; the most important of these alums are those of potassium, ammonium, and sodium.

'Selenic alums' have been prepared, in which sulphuric acid is replaced by selenic acid.

**Potassium alum**  $K_2SO_4 \cdot Al_2O_3 \cdot 3SO_3 \cdot 24H_2O$ . This salt occurs in nature as *kalinite* as an efflorescence, or in fibrous crystals on aluminous minerals, occasionally in octahedra, at Whitby, Campsie, &c. In the Solfatara, near Naples, and the islands of Volcano and Milo, it occurs in larger quantities, being formed by the action of volcanic gases upon feldspathic trachyte.

The manufacture of alum is of great antiquity. In the time of Pliny alum was in use as a mordant for the production of bright colours, and was even tested by means of the *tannin* in pomegranate juice to ascertain its purity. It was prepared in the thirteenth century at Smyrna from alum rock, and since the fifteenth century has been largely produced at Tolfa from the same substance.

Its preparation from pyritic shale has long been known, together with the fact that the presence of alkali was necessary to induce crystallisation, but, until proved in 1797 by Chaptal and Vauquelin, the essential presence of alkali in the crystals was not recognised.

Very pure alum is prepared in small quantities at Solfatara. The natural alum found there is digested with water in large wooden vats under cover, and maintained at about 40°C. by the natural heat of the soil. The solution is decanted and crystallised. A second crystallisation produces extremely pure alum.

A considerable amount of alum is prepared from alunite (*q. v.*, also *Aluminium sulphate*, art. ALUMINIUM). Alunite contains the elements of potassium alum, basic aluminium sulphate, and free alumina. In Sicily it is made into heaps and calcined in the open air. At Tolfa, where the manufacture is carried out on a larger scale, the roasting is conducted in furnaces like lime-kilns, lined with refractory materials. The mineral is heated in large pieces by the flame without direct contact with the fuel until sulphur dioxide begins to escape. The calcination requires about six hours, the mass losing about 35 p.c. of water. During the ignition, the excess of alumina beyond that necessary to produce alum is rendered insoluble, and no longer has the property of precipitating basic sulphates from the solution. The calcined mass is exposed to the air upon a clay floor for some weeks, during which time it is

occasionally moistened. The mud-like product is agitated in boilers with water at 70°C., and the clear decanted liquid, of density 10.12°B., is evaporated to 32°B., and crystallised in small wooden tubs. The crystals are cubic, opaque, and reddish from the presence of ferric oxide. This iron is, however, quite insoluble, and may be separated by recrystallisation; the soluble iron is said to be less than .005 p.c. In this way 'Roman alum' was formerly largely produced. On account of their great purity the red crystals were much sought after.

Alunite is now largely converted into alum by treatment with sulphuric acid and addition of potassium sulphate.

Guyot (C. R. 95, pp. 693 and 1,001; and C. N. 53, 27) has examined this process, and recommends the following method:—

On ignition of alunite, the free alumina is first rendered anhydrous, and soluble in sulphuric acid; at a higher temperature the basic sulphates become soluble, but if the temperature be allowed to rise too high the alumina becomes vitrified and is insoluble. Guyot recommends ignition at 800°C. for three hours as the best means of rendering the maximum amount of both these substances soluble. The composition of the calcined mass is determined, and acid is used in proportion to the amount of soluble sulphate contained. For a product of the following composition,  $K_2SO_4$ , 14.00 p.c.;  $Al_2O_3 \cdot 3SO_3$  (present as alum), 26.55;  $Al_2O_3 \cdot 3SO_3$  (free), 6.56;  $Al_2O_3$  (free), 18.58;  $OH$ , 11.90;  $Fe_2O_3$ , 0.80; silicious residue, 21.61 p.c., the proportions given below would be most satisfactory. Into a clay oven is poured 12.5 tons of sulphuric acid of 52°B. diluted to 30°B., and heated to 80° or 90°C. Eight tons of the calcined mineral is then added in portions and well stirred. After the whole has been added, the liquid is left for two hours, then evaporated to 38°B., and treated with 2.7 tons of potassium sulphate. The process up to this point occupies ten hours; after a further period of thirteen hours, the clear liquid is decanted off; its density should not exceed 42°B. The muddy liquid remaining is reduced to 24°B. by the addition of mother liquor from a previous crystallisation, stirred, allowed to settle, drawn off clear, mixed with the first decantate, and crystallised in a vat. After one day the crystals are removed, redissolved, and recrystallised. The muddy residue is crystallised out for a further crop of alum. The total yield of alum is about 2.3 times the original weight of ore. The insoluble matter contains 3.00 p.c. alumina and 2.01 p.c. potassium sulphate in addition to silica &c.

According to C. Schwartz (B. 17, 2, 387) the best temperature for the roasting is 500°C., and the acid used should have a density between 1.297 and 1.530.

The greater portion of the alum manufactured in England was formerly prepared from *alum shale* (*alum ore*), *alum schist*, and similar substances which occur in large quantities at Whitby in Yorkshire, Harlet and Campsie in Scotland, in Sweden, Thuringia, &c. These minerals are mixtures of aluminium silicate, iron pyrites, and bituminous substances; the iron pyrites is principally present in the aluminous schists as a fine black powder dissemi-



nated throughout the mass, and not distinguishable by the eye. The rapid oxidation of these minerals under atmospheric influences or heat is due to this fine state of division.

The following analyses by Richardson and Ronalds show the composition of the Whitby and Campsie shales:—

	Whitby		Campsie		
	Top rock	Bottom rock	Top rock	Top rock	Bottom rock
Sulphur . . . .	—	—	23.36	23.44	9.63
Iron . . . . .	—	—	18.16	15.04	
Ferric sulphide (pyrites) . .	4.20	8.50	—	—	—
Silica . . . . .	52.25	51.16	15.40	15.40	0.47
Ferrous oxide . .	8.49	6.11	—	—	2.18
Alumina . . . .	18.75	18.30	11.35	11.64	18.91
Lime . . . . .	1.25	2.15	1.40	2.22	0.10
Magnesia . . . .	0.91	0.90	0.50	0.32	2.17
Manganese peroxide . . . . .	trace	trace	0.15	—	0.55
Sulphuric acid . .	1.37	2.50	—	—	0.05
Potash . . . . .	0.13	trace	0.90	—	1.26
Soda . . . . .	0.20	trace	—	—	0.21
Chlorine . . . .	trace	trace	—	—	—
Carbon and loss .	—	—	29.78	—	—
Carbon only . . .	—	—	—	28.80	—
Coal . . . . .	4.97	8.29	—	—	8.51
Loss . . . . .	—	—	—	3.13	0.79
Water . . . . .	2.88	2.00	—	—	8.54
	95.40	91.39	100.00	99.99	100.00

*Aluminous carths* are friable, porous masses without structure, dark brown, and containing less silica than the schists. They usually occur in layers with lignite.

*Treatment of aluminous shale.*—The more earthy shales are porous, and, if piled in heaps in the open air and occasionally moistened, undergo spontaneous oxidation, and fall to pieces. Usually they require roasting, and, when not sufficiently bituminous for combustion, are first mixed with fuel. Thus, at Whitby and Hurlet the rock is laid in small pieces, in layers with brushwood or coal, upon a bed of well-pressed clay, and ignited. The top and bottom rock are usually mixed in order to ensure uniformity in the amount of combustible matter.

The shales at Campsie are too combustible, and require mixing with spent rock to retard the calcination.

At Salzweiler in Rhenish Prussia a stratum of brown coal beneath the ore was accidentally ignited in the mine in 1660, and has continued burning slowly up to the present time.

At Whitby the heaps are gradually increased as the mass burns until they reach a height of 90 or 100 feet and an area of 200 square feet. As, however, in these large heaps the temperature is liable to rise unduly and cause loss of sulphur, it is preferable, as at Hurlet, to limit the height and increase the area. At Whitby 130 tons of the calcined schist produce 1 ton of alum. Ores containing much lime cannot be used on account of the formation of calcium sulphate and consequent loss of material. Great care is necessary in regulating the heat. At too high a temperature a considerable amount of sulphur volatilises as sulphur dioxide, and is lost before its conversion into aluminium sulphate; the pyrites is liable to form a slag with the earthy matter and become useless, while the

aluminium sulphate itself becomes decomposed. When combustion is completed the mass occupies only about one-half its former bulk, is of a reddish tint and porous, allowing free access to air. During the atmospheric action, either by slow spontaneous oxidation or by combustion, the pyrites is decomposed. Sulphur is evolved, which combines with oxygen and attacks the clay, forming aluminium sulphate. At the same time the lower sulphide of iron remaining is converted into ferrous sulphate and ferric oxide. The calcined mass is usually kept for a considerable time before lixiviation.

*Lixiviation.*—The cisterns are of stone, or wood lined with lead, and are placed on different levels. The material is placed in the upper cisterns—the larger pieces above, the smaller pieces beneath—digested with water for six to twelve hours, and the liquid decanted into the lower cisterns. A second lixiviation is performed for an equal time with one-half the quantity of water and the liquor is used for the first digestion of a fresh charge of ore. The exhausted ore still contains a considerable amount of alumina and sulphuric acid. At Campsie the residues usually contain 12.7 p.c. alumina and 10.76 p.c. sulphuric oxide. The liquors of from 1.09 to 1.15 sp.gr. are allowed to deposit calcium sulphate, ferric oxide, &c., and are concentrated. The evaporation is preferably conducted at the surface on account of the deposition of a considerable quantity of solid matter containing much basic sulphate or iron, calcium sulphate, &c., during the evaporation. When, however, much magnesium sulphate is present, surface evaporation is not satisfactory on account of the formation of a crust of that salt which retards evaporation. In that case, as at Whitby, where also the amount of aluminium sulphate greatly exceeds that of ferrous sulphate, the evaporation is conducted in leaden pans to a density of 1.4 or 1.5.

At Hurlet and Campsie a reverberatory furnace is used. The bed is of stone, coated with well-rammed clay, 4 or 6 feet wide, 2 or 3 feet deep, 30 or 40 feet long. It is filled to the brim with strong liquor, and the flame and hot air from the fire carried over it. As evaporation proceeds, more liquor is added until the proper concentration is reached. It is then run into leaden pans, concentrated to about 1.4 sp.gr. and conveyed to a precipitating cistern containing the requisite quantity of dry potassium chloride; the liquid is well agitated and the chloride soon dissolves. In about 5 days the liquor is drained from the large crystals, which are washed and recrystallised. At Whitby 'alum meal' is first formed. The hot liquor, of sp.gr. 1.4 to 1.5, is mixed in a precipitating cistern with a saturated solution of potassium sulphate or chloride in the proper proportions, and the whole kept in constant agitation to induce the formation of small crystals. To ascertain the amount of potassium salt required, a known volume of the liquid is treated with potassium sulphate or chloride, left for 24 hours and the crystals slightly washed and weighed.

When much ferric sulphate is present in the solution, the addition of potassium sulphate would produce iron alum, isomorphous with ordinary alum, which would crystallise out and con-

taminate the product. The use of potassium chloride prevents this, by producing the easily soluble ferric chloride, while ferrous salts are converted into the equally soluble ferrous chloride, an equivalent amount of potassium sulphate being formed at the same time. Chloride of potassium is generally employed in preference to the sulphate, whenever sufficient iron sulphate is present to supply the requisite amount of sulphuric acid for the formation of alum; its greater solubility is also in its favour. At Whitley the proportion of iron is considerably less than would produce this effect. Too much chloride should be carefully avoided, for, after the iron sulphates have been decomposed, the aluminium sulphate is itself attacked with the production of the very soluble chloride, which is lost.

For the production of 100 parts of alum 18·3 parts of potassium sulphate, soluble in 10 parts of cold water or 15·6 parts of the chloride, soluble in 3 parts of cold water, would be required.

The *alum meal*, consisting of small brownish crystals, is drained and washed twice by agitation with cold water. The ferruginous solution and a little alum are thus removed and the meal is nearly pure. For recrystallisation, the meal is dissolved in the minimum quantity of boiling water and run into the 'rocking casks.' These are 5 feet high, 3 feet wide at the top and somewhat wider at the bottom, with movable staves.

After about 8 days the staves are removed and the alum found in a solid cake inclosing the solution. The liquid is removed by piercing the crust near the bottom and is added to a fresh quantity of the small crystals. At the bottom of each cask is found a slime consisting of an insoluble basic aluminium sulphate containing small crystals of alum.

The mother liquor from the alum meal has a sp.gr. of about 1·4; it contains sulphate or chloride of iron, magnesium sulphate, &c., and will yield more alum on evaporation. In a final evaporation it yields ferrous sulphate in fine green crystals. When iron is present in great quantity, the liquors are evaporated and the ferrous sulphate crystallised out before the addition of the potassium salt. In this case the iron salt is less pure and less soluble, but the alum subsequently produced contains less iron.

Formerly, potassium alum was alone produced. In 1845, however, the potassium sulphate was replaced by the ammonium sulphate produced from the then waste liquors from gas works, yielding ammonium alum. This great improvement was introduced by the late Mr. Peter Spence; his method was soon generally adopted both in England and on the Continent.

Another great advance was made by Mr. Spence in 1845 in the manufacture, by the treatment of the refuse shale underlying the coal seams of South Lancashire. This shale contains from 5 to 10 p.c. of carbonaceous matter. It is piled upon rows of loosely placed bricks (to allow a free passage to the air) in heaps 4 or 5 feet high and 20 feet long. The combustion is started with a little fuel, but the shale contains sufficient combustible matter to continue burning. The calcination is performed slowly at a heat below redness. In about 10 days the roasting is completed, the material has become soft, porous, and light red, whilst the

alumina contained in it has become anhydrous and soluble in sulphuric acid. Too high a temperature, however, partially vitrifies it, in which case it is only slowly attacked by acid. Charges of 20 tons are placed in large covered pans 40 feet long, 10 feet wide, and 3 feet deep, lined with lead, and are digested for about 48 hours with sulphuric acid (of sp.gr. 1·35) at 110°C., the temperature being maintained by fires beneath the boilers. Formerly ammonia was forced into the liquid from a boiler containing gas liquor; ammonium sulphate was thus produced, with considerable rise of temperature, and combined with the aluminium sulphate forming ammonium alum. The solution of alum so produced is run into cisterns 29 feet by 17 feet, and 1½ feet deep, in which it is kept in constant agitation. In about 14 hours the small crystals so formed are drained, washed with some mother liquor from 'block alum' and dissolved by a process known as 'rocking' for the production of pure block alum. For this purpose they are introduced into a hopper, at the bottom of which they encounter a current of steam at a pressure of 20 lbs. per sq. inch, both steam and crystals being supplied in such proportions that all the crystals are dissolved, while no steam is wasted. In this manner 4 tons of crystals may be dissolved in 30 or 40 minutes. The solution is run into a leaden tank, and, after a time, treated with a small quantity of size, which precipitates a quantity of insoluble matter. The clear liquid is next run into tubs about 6 feet high and 6 feet wide, tapering upwards, with movable lead-lined staves. After some days the staves are removed and a hole bored in the mass of crystals for the removal of the liquor. Each block weighs about 3 tons, while the mother liquor contains about 1 ton.

A great advantage of this process is the speed with which the crude material is converted into marketable alum. By the old process twelve months was required for this conversion, while by Spence's process the whole operation is performed in one month. For this process Mr. Spence was awarded the medal for alum manufacture at the Exhibition of 1862, at which date he manufactured 150 tons of alum weekly, over one half the total production of England (*v. Hofmann's report on Chemical Processes at the Exhibition of 1862*, p. 62, and *J. Carter Bell*, C. N. 12, 221).

Alum is also produced by the addition of potassium sulphate to aluminium sulphate, prepared by any of the processes already described. It is prepared in great purity from the sulphate produced from cryolite; 1 ton of cryolite produces three tons of alum (*v. Sodium aluminate*, art. ALUMINIUM).

Many other processes have been proposed and used for the preparation of alum.

Spence, in 1870 (Eng. Pat. 1,676), patented a method of preparing alum from mineral phosphates, especially that from Redonda near Antigua, which contains 26·1 p.c. of alumina as phosphate with ferric oxide and silica. It is calcined at a red heat to render it porous, powdered, and digested with sulphuric acid of sp.gr. 1·6 in quantity proportional to the amount of alumina, in lead-lined vessels, heated by steam. The liquid is concentrated to a density of 1·45 and

treated with the requisite amount of potassium sulphate to convert the whole of the alumina into alum. Phosphate containing 20 p.c. of alumina yields about  $1\frac{1}{2}$  times its weight of alum, from which, however, the last traces of phosphoric acid are removed with difficulty. The phosphoric acid in the mother liquors is valuable as a manure.

Methods have frequently been proposed for the preparation of alum from felspar. Ordinary felspar contains both potassium and aluminium combined with silica in larger proportions than are contained in alum; the problem to be solved is the substitution of sulphuric acid for silica. A method adopted by Turner, said to have been originated by Sprengel, consisted in the ignition of a mixture of one part of the powdered mineral with one part of potassium bisulphate until fused; one part of sodium carbonate was then added and the whole again fused. The mass was boiled with water and the insoluble double silicate remaining was decomposed by hot sulphuric acid of sp.gr. 1.20, and the alum crystallised out. On account of the high temperature required, this process was not successful.

For the more delicate dyes the alum used must be of extreme purity. Samples containing even less than 0.001 p.c. of iron may be unsuitable for certain purposes. The percentage of iron in alum or in aluminium sulphate is usually determined by means of a solution of ammonium thiocyanate standardised with iron alum. Many precautions are necessary in performing the analysis (*v. Tatlock*, S. C. I. 1837, 276).

Potassium alum crystallises in the cubic system, usually in fine large colourless octahedra of sp.gr. 1.735 (*Soret*, C. R. 99, 867). De Boisbaudran has also obtained it crystallised with hemihedral faces of the tetrahedron. The crystalline form is affected by the presence of other substances in solution, and by the temperature. When formed at ordinary temperatures in the presence of basic alum, the crystals are cubes, frequently dull on the surface from the presence of the basic salt; for this reason Roman alum usually forms cubes. At 40°C., even in presence of basic salts, octahedra are produced.

According to Poggiale (A. Ch. [3] 8, 467) the solubility of this salt and of ammonium alum is as follows:—

100 parts water dissolve:—

°C.	Crystallised Potassium Alum	Crystallised Ammonium Alum
0	3.9	5.2
10	9.5	9.1
20	15.1	13.6
30	22.0	19.3
40	30.9	27.3
50	44.1	36.5
60	66.6	51.5
70	90.7	72.0
80	131.5	103.0
90	209.3	187.8
100	357.5	

Potassium alum possesses a sweetish astringent taste and a strongly acid reaction. The aqueous solution decomposes when heated with precipitation of a basic alum, especially when

dilute. For this reason a small quantity, not sufficient to be distinguished by taste, is frequently added to impure water. The gelatinous precipitate carries with it the colouring matter and most of the organic impurities, producing a slimy deposit.

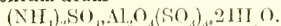
Alum is almost insoluble in a saturated solution of aluminium sulphate, and is quite insoluble in alcohol. On exposure to air, the crystals become white on the surface. This change is due, not to the loss of water, but to the absorption of ammonia from the air, with formation of a basic salt. Below 30°C. they lose no water; at 42° they evolve 11 molecules (*Juttke*, C. C. 18, 777). In a closed vessel over sulphuric acid they lose 18 molecules at 61° (*Graham*) and become slowly anhydrous at 100°, more rapidly in a current of air. When heated to dull redness they are converted into a porous friable mass, slowly soluble in water, known as 'burnt alum.' At a full-red heat alumina and potassium sulphate alone remain.

When potassium alum is mixed with one-third its weight of carbon and heated to redness, the residue is spontaneously inflammable on account of the presence of finely divided potassium sulphide, and is known as *Homburg's pyrophorus*. By fusing alumina with potassium bisulphate and digesting the mass in warm water, anhydrous potassium alum may be obtained in crystals of which 5 parts are soluble in 100 of water at 10°C. and 7.5 parts at 100° (*Salm-Horstmar*, J. Pr. 52, 319).

On the addition of caustic soda or sodium carbonate to a solution of alum until the precipitate at first produced is only just redissolved on agitation, *i.e.* when two-thirds of the acid has been neutralised, the solution contains a neutral basic alum, known as *neutral alum*, together with sodium sulphate. This solution, on account of the ease with which it gives up its excess of alumina to the fabric, is used by dyers as a mordant. Commercial potassium alum is frequently mixed with ammonium alum.

Alum is very largely used in the preparation of 'red liquor'; in the preparation of leather; as a size and weighting for paper; mixed with sawdust it is used as the fire-proof material of safes. See also *Austen* and *Wilber* (C. N. 51, 211).

#### Ammonium alum



occurs as *Tschermigite* in Bohemia. Ammonium alum forms crystals corresponding exactly with those of potassium alum, but is less soluble in water; insoluble in alcohol; sp.gr. 1.631 (*Soret*). The saturated solution boils at 110.6°C. and contains 207.7 pts. of the alum to 100 pts. of water (*Mulder*). When heated, the crystals swell and form a porous mass, losing water and sulphuric acid; at a high temperature alumina alone remains. In its general properties and uses it resembles potassium alum.

**Sodium alum**  $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2\text{O}_3(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Occurs as *menadozite* in S. America, and in Japan (*Divers*, C. N. 41, 218).

The crystals of this alum resemble those of other alums, but effloresce and fall to pieces in air. Their sp.gr. is 1.667 (*Soret*). At 16°C. 100 parts of water dissolve 110 parts of this alum. It is, therefore, difficult to crystallise and purify from iron. On account of the lower



cost of sodium salts it would be largely used in place of the other and more expensive alums, if it could be easily purified by crystallisation. Messrs. P. and F. M. Spence have patented a process with this object (Eng. Pat. 1881, 5,650).

#### Aluminium sulphate $Al_2O_3(SO_4)_3$ .

The bisulphate has been used by Becker (D. P. J. 257, 300), Suchoniel (S. C. I. 1887, 143) and others, for the purification of beet sugars. Becker prepares for this purpose a solution of sp.gr. 1.167 containing 4.37 p.c. alumina and 13.4 p.c. sulphurous oxide, by dissolving the hydrated oxide in sulphurous acid.

**Aluminium phosphates.** As hydrated phosphate aluminium occurs in the *turquoise*, and enters into the composition of *vecelite*, *lazulite* and *gibbsite*. It is found in considerable quantity in mineral phosphates, as in the Redonda phosphates which have been used for the preparation of alum and for fertilisers (v. ALUMS; MANURES). A massive stony variety is found on the hydrated oxide in Anguilla in the West Indies.

**Aluminium thiocyanate or sulphocyanate** has been proposed as a substitute for aluminium acetate for alizarin, steam reds, &c.; the colours produced are said to be especially permanent (v. Storeh and Ströbel, D. P. J. 241, 464, and Gottlieb Stein, D. P. J. 250, 36).

Lauber and Haussmann (D. P. J. 245, 306) recommend the following method of preparation: 5 kilos aluminium sulphate are dissolved in 5 litres boiling water, 250 grams of chalk are added, followed by 11.5 litres of crude calcium thiocyanate solution of 30°Tw., and the whole well stirred and allowed to settle. The clear liquid is ready for use.

#### Aluminium permanganate v. MANGANESE.

**Aluminium silicates.** These compounds are exceedingly numerous and important. As an anhydrous silicate, with silicate of iron, calcium, magnesium, &c., aluminium occurs in the varieties of *garnet*, crystallising in the regular system. As silicate of aluminium, calcium, and sodium it is found in *lapis lazuli*, which was formerly used as *ultramarine*. It is now replaced by artificial ultramarine (v. ULTRAMARINE). As silicate of aluminium, combined with potassium, iron, and magnesium, it occurs in the *micas*. As double silicate of aluminium, potassium, sodium, magnesium, or calcium, it forms the varieties of *felspar* which occur in immense quantities in eruptive rocks. By the decomposition of felspar by the carbonic acid in the atmosphere and in rain or spring water, the alkaline compounds are removed, leaving clay of more or less purity (v. CLAY), which, under pressure, becomes hardened and laminated, forming *shale*, and finally *slate* (q. v.). Many of the silicates of aluminium are of great importance, and of the widest application. The more important of them are specially considered under their applications (v. POTTERY; PORCELAIN).

**Aluminium acetate.** *Red liquor* (v. *Aluminium acetates*, art. ACETIC ACID).

The compounds of aluminium with the higher fatty acids are used for increasing the viscosity of mineral lubricating oils, under the names 'oil pulp' and 'fluid gelatin' (L. Marquardt, Fr. 25, 159).

**Aluminium oleate** is a soft white, putty-like substance, of great tenacity, insoluble in water,

soluble in ether and petroleum. A mixture of oleate, palmitate, and other fatty salts is produced from whale, cotton seed, and similar oils by saponification with soda and addition of the sodium salt so produced to a solution of alum. The gummy precipitate is known as 'oil pulp,' and is dissolved in 4 or 5 parts of mineral oil to form a 'thickener' for addition to the lubricator. A sample of oil-pulp resembling thick gelatin had a sp.gr. of 0.921, and contained 6 p.c. alumina combined with 30 p.c. fatty acids, together with 15 p.c. lard oil, and 48 p.c. paraffin oil (Oil and Colourman's Journ. 4, 403).

**Aluminium palmitate** is a constituent of oil pulp. It may be prepared in the same manner as the oleate, from palm oil. It forms a resinous, elastic, inodorous, neutral substance, insoluble in water, but readily soluble in petroleum and turpentine. K. Lieber (D. P. J. 246, 155) recommends the use of the latter solution as a varnish. It imparts a glossy appearance to paper, leather, &c., and renders them waterproof without affecting their elasticity.

**ALUNITE or ALUM STONE.** A basic sulphate of aluminium and potassium found chiefly in volcanic districts, viz. at Tolfa, near Civita Vecchia; at Solfatara, near Naples; at Puy de Garcey, Auvergne; and other localities. In most places it appears to have been formed by the action of volcanic exhalations upon trachytic rocks or breccias (A. v. Lasaulx, J. M. 1874, 142). The alunite of Breuil, Auvergne, however, seems to have been formed by the oxidation of iron pyrites or of marcasite contained in the clay.

The composition of alunite is shown in the following analyses:—

	Breuil, by Truchot	Tolfa, by Guyot
SO <sub>3</sub>	37.6	29.74
Al <sub>2</sub> O <sub>3</sub>	38.3	27.60
K <sub>2</sub> O	7.2	7.55
Fe <sub>2</sub> O <sub>3</sub>	trace	1.20
SiO <sub>2</sub>	8.2	22.71
OH <sub>2</sub>	8.5	11.20
	99.8	100.00

(v. ALUMINIUM).

#### ALUNOGEN. Native aluminium sulphate.

	SO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	M <sub>2</sub> O
a	36.935	13.479	2.883	0.157	0.140	0.133
b	34.685	15.198	—	—	—	—
c	34.43	15.52	—	—	—	—
	K <sub>2</sub> O	Na <sub>2</sub> O	In sol.	H <sub>2</sub> O		
a	0.87	0.131	0.235	45.109	= 99.299	
b	0.337	0.331	1.314	47.535	= 100	
c	—	—	7.62	42.56	= 100.13	

a. From mineral on shale, Nova Scotia (Adams, C. J. 40, 545).

b. Found as an efflorescence in New South Wales (Liversidge, J. Roy. Soc. N. S. W. 14, 213; C. J. 40, 591).

c. From Gila River, New Mexico (Clarke and Chatard, C. J. 48, 492; Am. S. 3] 28, 20 25) (v. ALUMINIUM).

#### ALVA or ALFA v. ESPARTO.

**ALVELOES.** A name applied to the *Euphorbia heterodoxa*, growing in Brazil, the juice of which is used as a cure for cancer (Ph. [3] 15, 614).

**AMADOU or GERMAN TINDER.** (*Amadou*, Fr.; *Zunderschwamm*, Ger.) A spongy combustible substance, prepared from a species of fungus, *Boletus igniarius*, which grows on the

trunks of cherry trees, ashes, beeches, &c. It must be plucked in the months of August and September. It may also be prepared from *Bleetus fomentarius*, another indigenous fungus, found on the oak and birch. It was formerly used in surgery, and has hence been called surgeons' agaric. Amadou is prepared by removing the outer bark and carefully separating the yellow-brown spongy substance which lies within it. This substance is cut into thin slices, and beaten with a mallet to soften it, till it can be easily pulled asunder between the fingers. In this state it is useful in surgery. To convert it into tinder, it is then boiled in a strong solution of nitre, dried, beaten anew, and put a second time into the solution. Sometimes, to render it very inflammable, it is imbued with gunpowder, whence the distinction of black and brown amadou.

**AMALGAM.** An alloy of mercury with some other metal or metals.

There are four general methods for preparing amalgams.

1. Metallic mercury is brought into contact with the other metal, either in the solid or in a finely-divided state at the ordinary, or at a higher temperature. In this way amalgams of antimony, arsenic, bismuth, cadmium, magnesium, potassium, silver, sodium, tellurium, thorium, tin, zinc, and lead may be obtained.

2. Mercury is brought into contact with a

saturated solution of a salt of the metal, when part of the mercury goes into solution and the remainder combines with the liberated metal; or better still, zinc or sodium amalgam is employed, when the zinc or sodium displaces the metal in the solution. By this method amalgams of bismuth, calcium, chromium, iridium, iron, magnesium, manganese, osmium, palladium, and strontium may be prepared by using sodium amalgam; and cobalt and nickel by using zinc amalgam (Moissan, C. R. 1879; C. N. 39, 84).

3. The metal to be amalgamated is placed in a solution of a mercury salt; copper may be amalgamated by this process.

4. The metal is placed in contact with mercury and dilute acid; this is the method usually employed in amalgamating zinc. Iron, aluminium, palladium, nickel, and cobalt may be made to combine with mercury by this process if they be placed in contact with a stick of zinc (Casamajor, C. N. 34, 36; Ar. Ph. [3] 11, 64; C. J. [2] 34, 171).

The combination of sodium with mercury by Method 1 takes place with great energy, heat and light being produced. It is best prepared by combining a small portion of the mercury with the sodium, and then adding the remainder to the amalgam.

Native amalgams are found in various parts of the world. The following table contains the analyses of a few:—

Ag	Hg	Au	Fe <sub>2</sub> O <sub>3</sub>	CaO	Ag <sub>2</sub> C	Fe	Zn	Pb	CaCO <sub>3</sub>	Cu	fusol. and loss	Formula	Locality	Analyst and Reference
75.900	24.065	—	—	—	—	—	—	—	—	—	0.490	Ag <sub>7</sub> Hg	Kongsberg, Norway.	Flügel, P. M. [5] 9, 146; C. J. [2] 38, 707.
92.454 36.0	7.195 64.0	—	0.033	0.055	0.088	—	—	—	—	—	1.328	Ag <sub>12</sub> Hg	Moschellandsberg Palatinate.	Klaproth, Ure 1.
25.0 27.5	73.3 72.5	—	—	—	—	—	—	—	—	—	—	—	Allemont, Dauphine.	He-cr, id. Cordier, ib.
46.30	51.12	—	—	—	—	0.18	tr.	tr.	0.21	—	1.01	—	Sälagrube, Sweden.	Nord-bröm, J. 35, 1, 521.
56.70	43.27	—	—	—	—	—	—	—	—	tr.	—	—	Friedrichslegen-Mine.	Weiss, J. 36, 1828; Z. geol. Ges. 34, 817.
—	60.98 to 58.37	39.02 to 41.63	—	—	—	—	—	—	—	—	—	—	Mariposa, California.	Ure.
5.00	57.40	38.39	—	—	—	—	—	—	—	—	—	( $\frac{1}{2}$ Au) <sup>4</sup> Ag <sub>7</sub> Hg <sub>5</sub>	Choco, New Grenada.	Schneider, Ure.

Gold and silver in the metallic state are extracted from their ores by grinding the ores and making them pass through mercury. (For details v. these metals, and May, S. C. I. 4, 252; Moon, *id.* 4, 678; Miller, *id.* 4, 122; Whitehead, *id.* 4, 503; Fisher and Waber, *id.* 4, 351; Barker, D. P. J. 251, 32; Body, *id.* 252, 33; Molloy, *id.* 254, 210; Bonnet, *id.* 254, 297; Cassel, *id.* 257, 286; Jordan, *id.* 258, 163; Hollick, *id.* 258, 168.) When the mercury has taken up a quantity of gold, the amalgam is squeezed through chamois leather, when the greater portion of the gold is left, combined with a little mercury, as a pasty mass. Kazantseff (Bl. [2] 30, 20; C. J. [2] 34, 937) finds that the mercury which escapes contains at ordinary temperatures 0.126 p.c. of gold, at 0° 0.110 p.c. and at 100° C. 0.650 p.c. thus behaving like an aqueous solution.

Berthelot also finds that the solution of defi-

nite amalgams in different quantities of mercury, like the solution of salts in water, absorbs a constant amount of heat; thus the heat of solution of Hg<sub>7</sub>K in four times its weight of mercury is -8.0 kil. deg. of heat, and in twenty times -9.0 kil. deg. (C. R. 89, 465; C. J. [2] 38, 1).

According to Berthelot the maximum heats of formation for amalgams of potassium and sodium are 34.2 and 21.1 corresponding with Hg<sub>7</sub>K, a crystalline compound containing 1.6 p.c. of potassium, and Hg<sub>12</sub>Na containing 2 p.c. of sodium. In these amalgams the relative affinities of the free alkali metals are inverted: this explains Kraut's and Popp's observation that sodium displaces potassium when potassic hydrate is treated with sodium amalgam, the final result being the formation of Hg<sub>12</sub>Na (C. R. 88, 1,335).

Wiedemann states (W. [2] 3, 237-350; C. J. [2] 34, 466) that the specific heats of tin and of its amalgams SnHg Sn<sub>2</sub>Hg are nearly the same at

high temperatures, which would be the case if it be assumed that the specific heats of alloys are the mean of their components; but  $\text{SnHg}$  at  $128^\circ\text{C}$ . and  $\text{Sn}_2\text{Hg}$  at  $164^\circ\text{C}$ . behave like a mixture of a solid and a liquid.

By heating alloys of mercury to the boiling-points of sulphur, mercury, and diphenylamine, Sonza (B. 9, 1050) obtained amalgams represented by the formula in the annexed table:—

Sulphur vapour	Mercury vapour	Diphenylamine vapour
$\text{Au}_2\text{Hg}$	$\text{Au}_2\text{Hg}$	$\text{Au}_2\text{Hg}$
$\text{Ag}_{12}\text{Hg}$	$\text{Ag}_{11}\text{Hg}$	$\text{Ag}_2\text{Hg}$
$\text{Cu}_4\text{Hg}$	$\text{Cu}_{11}\text{Hg}$	$\text{Cu}_{11}\text{Hg}$
$\text{K.Hg}^*$	—	—
$\text{Na}^3\text{Hg}$	—	—
	$\text{Pb}_2\text{Hg}$	—

But according to Merz\* and Weith amalgams of gold, silver, copper, lead, tin, bismuth, cadmium, and zinc lose their mercury if kept at these temperatures for some hours. Potassium and sodium also slowly part with mercury (B. 14, 1,138; C. J. 40, 881). 'Ammonium amalgam' is prepared by acting on a saturated solution of ammonium chloride with sodium amalgam; the amalgam thus obtained soon breaks up into mercury, and ammonia, and hydrogen gases. According to Wetherill (Am. S. [2] 50, 160) this compound is not a true amalgam, as when an ammoniacal solution is electrolysed, the negative pole being a spongy plate impregnated with mercury, no amalgam is formed. Landolt (Z. [2] 5, 429) draws attention to the fact that ammonium amalgam does not reduce solutions of silver nitrate, ferric chloride, or cupric sulphate, as do sodium and potassium amalgams.

Seeley (C. N. 21, 265) has shown that on submitting ammonium amalgam to pressure, its volume diminishes in the same way that gases do, and hence he considers that the ammonia and hydrogen exist in the amalgam as gas, and that the spongy mass is only a froth of mercury inclosing these gases.

Gellatlin (Z. [2] 5, 607) asserts that when ammonium amalgam, free from sodium, is placed in contact with phosphorus, phosphuretted hydrogen is evolved, and he infers that the hydrogen must be in the nascent state.

Pfeil and Lippmann (C. R. 62, 426) state that trimethylamine hydrochloride also forms a spongy amalgam which quickly decomposes with evolution of hydrogen and formation of trimethylamine; saturated solutions of the hydrochlorides of aniline, coniine, morphine, and quinine give off hydrogen only.

**Electrical amalgam** is made by melting together 1 part of zinc and 1 part of tin, and then adding 3 parts of mercury.

**Silvering amalgams.** For metals, 1 part of silver to 8 parts of mercury; for glass, 1 part each of lead and tin, 2 parts bismuth, and 4 parts mercury.

**Tooth cements.** 1. A gold amalgam containing enough mercury to make it doughy at the temperature of boiling water. 2. One part of zinc filings and 2 parts of mercury, mixed and applied at once. 3. Amalgam containing 0.25 to 0.30 of copper.

**AMANITA MUSCARIA.** *Agaricus muscarius*, *Fly agaric*. A poisonous fungus, used in Kamtschatka and Siberia as a narcotic and intoxicant,

\* A crystalline compound with a silvery lustre.

and, when steeped in milk, as a fly poison. A narcotic organic base, *muscarine*,  $\text{C}_5\text{H}_{13}\text{NO}_3$ , which is the hydrated aldehyde of betaine, has been isolated from it (Schmiedeberg and Harnack, J. 1876, 894).

**AMARANTH** v. Azo-COLOURING MATTERS.

**AMAZON STONE.** A variety of orthoclase, found at Lake Ilmen, Russia, of a bluish-green colour; and at Baikal, Siberia, in silvery spangles on a green base. The colouring matter is said to be due to organic iron salts (König, J. 30, 1,333). Used for making trinkets.

**AMBAR, LIQUID.** A resin obtained from *Liquidambar styraciflua* growing in Louisiana and Mexico. It is of the consistence of turpentine, has a brown ash grey colour, dries up readily, smells like gum benzoïn, has a bitter sharp burning taste, is soluble in 4 parts of alcohol. It contains 1.4 p.c. benzoic acid.

**AMBER.** *Ambre, Succin*, Fr. *Bernstein, Electrum, Agtstein, gelbes Erdharz*, Ger. The fossil resin of the *Pinites succinifer*, found on the southern coast of the Baltic, in the diluvial soils of Prussia, in Saxony, Poland, Sicily, and Maryland, U.S. The amber-bearing stratum of the Baltic lies partly below the sea level; it consists of a coarse green sand, the particles of which are covered with a yellow coating. Amber is found in it to the extent of one kilogram per 20 cubic feet.

Amber is a hard, brittle, tasteless substance, usually semi-transparent or opaque, and of a glassy surface; it is found in all colours, but most commonly yellow or orange; it frequently contains leaves and insects. Statements differ as to its sp.gr.: Helm (Ar. Ph. [3] 11, 229, 246; C. J. [2] 34, 323) gives it as varying between 1.05 and 1.095; Ure, between 1.035 and 1.070; Reboux (A. Ch. [5] 9, 138, 144; C. J. [2] 32, 903), between 1.09 and 1.11. Its hardness varies from 2 to 2.5. Its fracture is conchoidal, and it is susceptible of a high polish. It is worked on a lathe with whiting and water or rotten stone and oil, and finished off by friction with a flannel. A large amount of electricity is thus generated, and the amber is apt to splinter. Amber is mended by smearing the fracture with linseed oil, pressing the pieces firmly together, and holding over a charcoal fire. Amber is coloured by placing it in linseed oil coloured with dragon's blood, alizarine, purpurine, or indigo, heating to  $190-200^\circ$ , and, after keeping the temperature steady for a few minutes, allowing to cool slowly. If heated in a fluorescent oil the amber becomes fluorescent (Hanausek, C. C. 15, 461; S. C. I. 3, 491; Ph. [3] 14, 566). Amber is soluble in alkalis without decomposition, colours sulphuric acid purple, and is soluble in chloroform.

According to Helm (l.c.), Prussian amber contains from 17 to 22 p.c. of a substance melting at  $105^\circ\text{C}$ ., soluble in alcohol; 5 to 6 p.c. of a substance melting at  $145^\circ$ , insoluble in alcohol, but soluble in ether; 7 to 9 p.c. of a body melting at  $175^\circ\text{C}$ ., insoluble in alcohol and ether, but dissolving in caustic potash; 44.60 p.c. of an insoluble bitumen,  $\text{C}_{10}\text{H}_{10}\text{O}$ , having the composition of ordinary camphor; and 3.2 8.2 succinic acid.

Clear yellow amber has no characteristic appearance under the microscope, but the opaque



or white variety under 200 500 diameters is seen to be full of round cavities. Amber contains sulphur, the quantity ranging from 0.26 to 0.34 p.c. (Helm, Ar. Ph. [3] 13, 496; C. J. [2] 31, 300). John. (J. 1876, 1272) gives the following analyses of amber:—

C.	H.	O.	S.
80.75	10.02	9.23	0.36
80.29	10.57	9.14	0.32

A solution of amber (1 kilo in 2 kilos of chloroform) has been applied to silken goods to give softness and elasticity (O. Thummel, S. C. I. 2, 378). Amber is valued by Turks and other Orientals as a charm against infection. Its chief use in England is in jewellery and for mouth-pieces to pipes.

Natural amber when rubbed has an aromatic odour, which copal and 'mellite' (artificial amber) do not possess. Natural amber, when greased and warmed, can be bent, but copal and mellite will not bend under this treatment. Copal melts at a low temperature, changes colour at 100°C. and loses water; natural amber does not melt at 400°, but blackens and gives off a suffocating gas; it also burns with a yellow flame, leaving a light lustrous coal. 'Mellite' is infusible and leaves a white residue. Natural amber is harder than artificial amber, and resists the pressure of the finger nail. Reboux, A. Ch. [5] 9, 138; C. J. [2] 32, 903; C. N. 37, 31; and Cooley, 1; v. also RESINS.

**AMBER, OIL OF.** When amber is heated it softens, fuses, and gives off succinic acid, water, oil, and a combustible gas. If the residue (colophony of amber) be more strongly heated, a colourless oil passes over. These oils, according to Pelletier and Walter (A. Ch. [3] 9, 89) have the composition of oil of turpentine. By distilling with water, a pale yellow oil, having a strong odour and acrid taste, can be obtained. It blackens and thickens on exposure to air and heat, boils at 86°, and has a sp.gr. of .758 at 24°. One part of the rectified oil mixed with 24 parts alcohol (0.830) and 96 of caustic ammonia, forms *eau de luce*, a celebrated old perfume. By mixing 'eau de luce' with nitric acid, artificial musk is made. Its solution in alcohol was formerly considered as a specific for whooping-cough (v. also RESINS).

**AMBER VARNISH** v. VARNISH.

**AMBERGRIS.** (*Ambregris*, Fr.; *Ambra*, *Ambar*, Ger.) Is found in the sea, near the coasts of tropical countries, and in the intestines of the spermæti whale (*Physeter macrocephalus*).

Ambregris is generally found in fragments, but a piece has been obtained weighing 225 lbs. Its sp.gr. ranges from 0.780 to 0.926 (.780 to .896 Brande, .908-.920 Pereira). If of good quality, it adheres like wax to the edge of a knife with which it is scraped, retains the impression of the nails, and emits a fat odorous liquid on being penetrated with a hot needle. It is generally brittle, but on rubbing it with the nail it becomes smooth like hard soap. Its colour varies from black to white. Its smell is peculiar, and not easily counterfeited. It melts at 62-2°C., at 100°C. it is volatilised as a white vapour; on a red-hot coal it burns and is entirely dissipated. Water has no action on it; acids, except nitric acid, act feebly upon it; ether and the volatile oils dissolve it; so do

the fixed oils, and also ammonia when assisted by heat; alcohol dissolves a portion of it.

The principal constituent of ambregris is *ambreña*; its inorganic constituents are carbonate and phosphate of calcium, with traces of ferric oxide and alkaline chlorides.

Used by perfumers. The Chinese test its purity by scraping it upon boiling tea, in which it should dissolve (Ure).

**AMBLYGONITE.** A greenish-coloured mineral, marked on the surface with reddish and yellowish brown spots, translucent, brittle, intumesces and fuses to a white enamel.

P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	Li <sub>2</sub> O	Na <sub>2</sub> O	K <sub>2</sub> O	F	Fe <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O
a. 47.15	88.43	7.03	3.29	9.43	8.11	—	—
b. 39.00	25.66	—	—	—	—	1.71	—
c. 48.20	31.83	10.18	—	—	6.45	—	3.06

a. From Chursdorf and Armsdorf, Pinig, Saxony, Handwb. d. Chem. 2 Auf. 1, 665; Dana, 2, 409.

b. Thenard, M. S. [3] 9, 1,175; J. 32, 1,204.

c. Rammelsberg, J. M. 1883, 1, 11; J. 36, 1865. Thenard (*L.c.*) uses this mineral for the manufacture of superphosphates (v. also LITHUM).

**AMBREIN.** *Ambreine*, Fr. *Ambarstoff*, Ger. Isolated by Pelletier and Cavoutou, by digesting ambregris in hot alcohol, sp.gr. 0.827. It is of a brilliant white colour, has an agreeable odour, is destitute of taste, is insoluble in water, dissolves readily in alcohol and ether. Melts at 30°C., and is volatilised above 100°C.; is non-saponifiable; is converted by nitric acid into *ambreic* acid. Ambrein is probably impure cholesterol. Pelletier (A. 6, 24) found it to contain 83.3 p.c. C, 13.3 H, and 3.31 p.c. O.

**AMBRITE** v. RESINS.

**AMBROSINE.** A resinous mineral found in the phosphatic beds near Charleston, South Carolina, U.S.

**AMERICAN COW or MILK TREE WAX** v. WAX.

**AMERICAN ELEMI** v. OLEO-RESINS.

**AMEHYST.** Tetramethyl saffranine and tetra-amyli saffranine are found in commerce under this name (v. AZINES).

**AMETHYST, ORIENTAL.** v. CORUNDUM.

**AMIANTHUS.** (*Amiante*, Fr.) *Mountain flax*. The whiter and more delicate varieties of asbestos, particularly those possessing a satiny lustre. A variety found at Oisans, France, is somewhat elastic (v. ASBESTOS).

**AMIDE POWDER.** An explosive similar to ordinary gunpowder, in which, in place of the sulphur, an ammonium salt is employed in combination with saltpetre, in such proportions that on ignition potass-amide, volatile at high temperatures, is formed. This increases the useful effect of the explosive, which burns without residue (Gaens. Eng. Pat. 14, 412, 1885; S. C. I. 5, 678).

**AMIDOAZOBENZENE or ANILINE YELLOW** v. AZO-COLOURING MATTERS.

**AMIDOGENE.** An explosive made by dissolving 73 parts of potassium nitrate and 1 part magnesium sulphate in one third their weight of boiling water; 8 parts of ground wood charcoal, 8 parts of bran, and 10 parts of sulphur are added, and the whole is digested for two hours at 140°; it is then dried at 50° and made into cartridges (Gempeler, S. C. I. 3, 191; 1, 201; Biedermann's Chem. Tech. Jahrb. 7, 116).

**AMIDONAPHTHOPHFNAZINE** *v.* AZINES.**AMIDOPHENOPHENANTHRAZINE** *v.*

AZINES.

**AMLAKI** (Beng.), **ANVULA** (Hind.), **AWLA** (Bomb.), **TOPPI** (Tamil). The fruit of *Phyllanthus emblica* (emblic myrobolams), used in a fresh condition as a laxative, and, when dried, as an astringent (Dymock, Ph. [3] 10, 382).

**AMMIOLITE**. A red earthy mineral from Chili, containing:

Sb	Te	Cu	Hg	SiO <sub>2</sub>
36.5	14.8	12.2	22.2	2.5

(Rammelsberg, Mineralchemie, 423).

**AMMONIA**. *Volatile alkali*; *Alkaline air*; *Spirit of hartshorn*, NH<sub>3</sub>. Solutions of ammonia have been known from very early times, but the substance itself was first clearly recognised by Priestley, who obtained it by boiling the aqueous solution and collecting the gas, which he termed *alkaline air*, over the mercurial pneumatic trough. Scheele proved that it contained nitrogen, and Berthollet, and, more accurately, Austin, demonstrated its real nature and determined the properties of its constituents.

Ammoniacal salts are found in small quantity in the air and in most natural water; in the juice of plants, in most animal fluids, and in many soils, and in a few minerals, ochres, clays, marls, &c. Ammonia can be synthetically obtained in small quantity by the action of the silent discharge on a mixture of nitrogen and hydrogen (Donkin, P. 21, 281), or as nitrite by means of a strong induction spark, or a mixture of nitrogen and water vapour (Thenard, C. R. 76, 938); or as chloride, by passing electric sparks through a mixture of hydrogen chloride, nitrogen, and hydrogen (Deville, C. R. 60, 317); or by the action of heated spongy platinum, pumice, &c., on a mixture of hydrogen and nitric acid.

(For other methods *v.* WATTS' DICTIONARY vol. i. 196.)

For laboratory purposes ammonia gas is usually prepared by heating the aqueous solution, or by heating a mixture of ammonium sulphate or chloride and slaked lime. The gas is dried by passing over quicklime. For the preparation of absolutely pure ammonia *v.* Stas, Fr. 6, 423.

Ammonia is a colourless gas, which, when perfectly dry, is without smell; it is poisonous when breathed in quantity and destroys the mucous membrane. It is very feebly combustible in air, especially when heated, and may be made to burn readily in oxygen gas. It is easily condensed to a mobile colourless and very expansive liquid of sp.gr.  $\frac{0.6234}{0.6362}$  at  $\frac{0^\circ}{0^\circ}$  (Jolly) which

boils at  $-33.7^\circ$  (Bunsen) and freezes to a white crystalline mass at  $-75^\circ$  (Faraday).

According to Bunsen (P. 46, 95) the vapour tension of this liquid is:—

At $-33.7^\circ$	1	atmos.
0°	4.4	„
+ 15.5°	6.9	„
+ 2.8°	10	„

(Compare Regnault, J. 1863, 66).

Liquid ammonia dissolves the alkali metals without change, forming blue solutions; it has no action on oil of vitriol at  $65^\circ$  (Gore, C. N. 23, 251). Ammonia gas is gradually decomposed into its elements even at  $500^\circ$ , and to a greater extent at higher temperatures, and especially

by the disruptive discharge from a powerful Ruhmkorff coil; in no case, however, is the decomposition by heat complete.

Ramsay and Young (C. J. 45, 92) find that when the gas is passed through a heated porcelain tube or an iron tube, or glass tube filled with asbestos cardboard, the amount of decomposition at  $500^\circ$ – $520^\circ$  is nearly equal and very small. In contact with a glass surface, the temperature at which decomposition begins is much higher. Ammonia may indeed be heated to  $700^\circ$  in contact with glass without any appreciable decomposition. The nature of the heated surface has a very great influence on the extent of the decomposition.

When the gas is passed over certain metals, *e.g.* platinum, gold, silver, iron, copper, it is decomposed in its elements; when heated with potassium it forms the *potassamines* NH<sub>4</sub>K and NH<sub>4</sub>Na; titanium and boron heated in the gas form the respective nitrides. A mixture of ammonia and air passed over heated copper turnings yields pure nitrogen gas and water.

A heated platinum wire suspended in a mixture of ammonia and oxygen, or air, yields ammonium nitrite and nitrate. (For other reactions *v.* WATTS' DICTIONARY vol. i. 198.)

Ammonia is very soluble in water, alcohol, and ether, and in many saline solutions.

1 gram of water at  $0^\circ$  absorbs 1,148 cc. or .875 gram of ammonia at  $0^\circ$  and 0.76 m. pressure. At  $10^\circ$ , 0.679 gram; at  $20^\circ$ , 0.526; at  $30^\circ$ , 0.403; and at  $100^\circ$ , .074 gram (Roscoe and Dittmar, C. J. 12, 128).

The aqueous solution is a pungent-smelling, caustic, alkaline liquid, which solidifies at  $49^\circ$  to an inodorous crystalline mass. In the act of solution considerable heat is evolved; according to Thomsen, NH<sub>3</sub>.Aq = 8,430 calories. The concentrated solution diluted with water also evolves heat. When dissolved under pressure and at ordinary temperatures more of the gas is taken up than corresponds with Dalton and Henry's law; at  $100^\circ$ , however, the amount dissolved under pressure of more than 1 atmos. is in accordance with the law (Sims, C. J. 14, 1). The strongest aqueous solution of ammonia has a sp.gr. 0.884 at  $64^\circ$  (Carius) and contains 36 p.c. NH<sub>3</sub>. It has been generally assumed that the aqueous solution contains the hydroxide NH<sub>4</sub>OH, corresponding to KHO and NaHO, but the thermal observations of Thomsen and Tommasi appear to throw doubt on the existence of ammonium hydroxide.

The solution dissolves many metallic oxides, *e.g.* Ag<sub>2</sub>O, CuO, and certain salts, *e.g.* AgCl, Ag<sub>2</sub>PO<sub>4</sub>, which are insoluble in water. It also dissolves many fats and resins.

In contact with red-hot coke or coal, ammonia forms ammonium cyanide and hydrogen, together with, under certain conditions, marsh gas and acetylene. Chlorine, bromine, and iodine at once decompose ammonia, forming nitrogen and a haloid salt; and with the occasional production of explosive compounds, *e.g.* nitrogen trichloride NCl<sub>3</sub>, and diamine di-iodide N<sub>2</sub>H<sub>4</sub>I<sub>2</sub>.

With many of the inorganic and organic anhydrides and with the acid chlorides it forms the ammonium salts of the corresponding amic acid. Thus with carbon dioxide it yields ammonium carbamate;  $2\text{NH}_3 + \text{CO}_2 = \text{CO.NH}_4\text{ONH}_2$ .

Certain salts, *e.g.* calcium chloride, silver chloride, zinc chloride, copper sulphite, ammonium nitrate, combine with ammonia to form stable compounds from which the gas can

be expelled by heat. It was by heating the compound  $2\text{AgCl}\cdot 3\text{NH}_3$  in a sealed tube that Faraday, in 1823, first effected the liquefaction of ammonia.

DENSITY OF AQUEOUS SOLUTION OF AMMONIA AT  $15^\circ$  (LUNGE AND WIERNIS).

Sp-gr.	$\text{NH}_3$ p.c.	1 litre con- tains $\text{NH}_3$ g.	Correction of sp-gr. for $\pm 1^\circ$	Sp-gr.	$\text{NH}_3$ p.c.	1 litre con- tains $\text{NH}_3$ g.	Correction of sp-gr. for $\pm 1^\circ$
1.000	0.00	0.0	0.00018	0.940	15.63	146.9	0.00039
0.998	0.15	4.5	0.00018	0.938	16.22	152.1	0.000.0
0.996	0.91	9.1	0.00019	0.936	16.82	157.4	0.00041
0.994	1.37	13.6	0.00019	0.934	17.42	162.7	0.00041
0.992	1.84	18.2	0.00020	0.932	18.03	168.1	0.00042
0.990	2.31	22.9	0.00020	0.930	18.64	173.4	0.00042
0.988	2.80	27.7	0.00021	0.928	19.25	178.6	0.00043
0.986	3.30	32.5	0.00021	0.926	19.87	184.2	0.00044
0.984	3.80	37.4	0.00022	0.924	20.49	189.3	0.00045
0.982	4.30	42.2	0.00022	0.922	21.12	194.7	0.00046
0.980	4.80	47.0	0.00023	0.920	21.75	200.1	0.00047
0.978	5.30	51.8	0.00023	0.918	22.39	205.6	0.00048
0.976	5.80	56.6	0.00024	0.916	23.03	210.9	0.00049
0.974	6.30	61.4	0.00024	0.914	23.68	216.3	0.00050
0.972	6.80	66.1	0.00025	0.912	24.33	221.9	0.00051
0.970	7.31	70.9	0.00025	0.910	24.99	227.4	0.00052
0.968	7.82	75.7	0.00026	0.908	25.65	232.9	0.00053
0.966	8.33	80.5	0.00026	0.906	26.31	238.3	0.00054
0.964	8.84	85.2	0.00027	0.904	26.98	243.9	0.00055
0.962	9.35	89.9	0.00028	0.902	27.65	249.4	0.00056
0.960	9.91	95.1	0.00029	0.900	28.33	255.0	0.00057
0.958	10.47	100.3	0.00030	0.898	29.01	260.5	0.00058
0.956	11.03	105.4	0.00031	0.896	29.69	266.0	0.00059
0.954	11.60	110.7	0.00032	0.894	30.37	271.5	0.00060
0.952	12.17	115.9	0.00033	0.892	31.05	277.0	0.00060
0.950	12.74	121.0	0.00034	0.890	31.75	282.6	0.00061
0.948	13.31	126.2	0.00035	0.888	32.50	288.6	0.00062
0.946	13.88	131.3	0.00036	0.886	33.25	294.6	0.00063
0.944	14.46	136.5	0.00037	0.884	34.10	301.4	0.00064
0.942	15.04	141.7	0.00038	0.882	34.95	308.3	0.00065

**Technical sources of ammonia.**<sup>1</sup>—Ammonia is formed in nature principally during the decay of nitrogenous organic substances. Thus very considerable quantities of it exist, both in the soil and in the atmospheric air, but, extremely important as this occurrence is for agriculture, it is only quite exceptionally possible to utilise it for the recovery of ammoniacal compounds. That object is practically attained almost entirely by the destructive distillation of organic substances, chiefly coal.

**A. Natural occurrence of ammoniacal compounds, in sufficient quantity to be of commercial value.**—Ammonium carbonate has been found in *guano deposits* on the West Coast of South America, and has been exported to Europe. A sample, introduced into Germany in 1848, consisted essentially of ammonium bicarbonate mixed with some insoluble matter. Ammonium sulphate is contained in the Tuscan 'soffioni,' and is obtained there in somewhat considerable quantities as a by-product in the manufacture of boric acid. Ammonium chloride, together with sulphate, is sometimes collected in the neighbourhood of *volcanoes*.

**B. Ammonia made from hydrogen and atmospheric nitrogen.**—The fact that nitrogen and hydrogen can be united by the electric discharge, or by contact with certain substances, has been made use of by inventors, but, in spite of very confident assertions to the contrary, those reactions have never turned out to be practicable; nor has the intervention of boron or titanium proved more successful. It is very doubtful if the ammonia said to have been ob-

tained by some of those processes has not been pre-existent in the materials employed, or is due to the nitrogen contained in the coke employed, and it is certain that none of it has ever found its way into commerce. In order to give an outline of the attempts hitherto made in this direction, we enumerate the following patented processes:—

Swindells (E. P. June 21, 1876) passes a mixture of air and steam over red-hot coal and then through a solution of caustic soda.

Rickman (E. P. 3,341, 1878) proposes to manufacture ammonia from the nitrogen of atmospheric air, by injecting a mixture of steam and air into retorts filled with coke, spongy iron, or the like, heated to about  $550^\circ$ . The steam is decomposed by those oxidisable substances, hydrogen being liberated, which is supposed to combine with the nitrogen of the air to form ammonia. Comp. also the German Patent, No. 10,889, by Rickman and Thompson.

G. Th. Glover (E. P. 1,890, of 1880) passes furnace gases mixed with steam and hydrogen chloride over coal or bituminous shale heated to redness, whereby ammonium chloride is supposed to be formed.

Solvay (Bl. 25, 527 and Wagner (J. 1876, 444) tried coke impregnated with magnesium chloride and heated by a blast.

Basset (E. P. 4,338, 1879) employs coal impregnated with boric acid over which nitrogen is passed; the boron nitride is then decomposed by steam. G. N. Tucker (G. P. 13,392) proceeds in a somewhat similar way.

G. S. Johnson (C. N. 43, pp. 42 and 288) passes nitrogen mixed with hydrogen through red-hot spongy platinum.

<sup>1</sup> Comp. G. Lunge's Coal Tar and Ammonia (Gurney and Jackson, 1887), chapters xii.-xiv.



Th. G. Young (E. P. 1700, 1830) passes the electric current through a mixture of 3 vols. of hydrogen and 1 vol. nitrogen.

Several other inventors invoke the aid of electricity for combining nitrogen and hydrogen; thus Müller and Geisenberger (G. P. 11,489 and 12,364), and the Société l'Azote (G. P. 17,070). The latter proposes obtaining both nitrogen and hydrogen by the action of melted zinc on air and steam in separate furnaces, zinc oxide being formed at the same time in each case. The two gases are to be combined by spongy iron impregnated with titanium or else by platinated carbon, and this combination is to be promoted by an electric current.

Twinch (E. P. 3,712, 1881) patents the manufacture of ammonia by the joint action of atmospheric air, steam, nitric oxide, and caustic soda.

*C. Ammonia made from cyanides, prepared by means of atmospheric nitrogen.*—Margueritte and Sourdeval (E. P. 1,027, 1860) patented a process for manufacturing ammonia, consisting in first preparing cyanides by heating a mixture of barium carbonate and coal in an atmosphere of nitrogen, and afterwards decomposing the cyanides by steam. This process, which did not prove successful in their hands, has been taken up by L. Mond (E. P. 433, 1882). He forms lumps, or bricks, *e.g.* by compressing a mixture of 32 parts of barium carbonate, 8 of wood-charcoal and 11 of coal-tar pitch, or in some other suitable way. These lumps are first heated in a reducing flame till the pitch has been converted into coke, and the barium carbonate has been partially or entirely converted into oxide. They are then charged into an annular kiln of the usual description, where they are first exposed at a temperature of  $1400^{\circ}\text{C}$ . to a current of gases containing as much nitrogen and as little  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{O}$  as possible. When a sufficient quantity of cyanides has been formed, the current of hot gases is shut off and a cold current of the same composition is passed through the mass till the temperature has fallen to  $500^{\circ}$ , when steam is admitted to decompose the cyanides into ammonia which is collected in the usual way. This process, although tried on a somewhat large scale, has not yet come into practical operation, and is, therefore, probably at this moment not yet worked out so as to be fully successful. No more can be said of the processes of L. Q. and A. Brin (E. P. 3,089, 1883), J. Young (E. P. 16,046, 1885), and T. B. Fogarty (E. P. 5,361, 1883).

*D. Ammonia from urine, sewage, and animal excreta.*—Urine is not merely the oddest, but for centuries was the only source for obtaining ammonia compounds on a commercial scale. It is stated that sal-ammoniac made from it was an article of commerce as early as 1410, and that the Jesuit Sicaud in 1720 saw the manufacture of it in the Delta of the Nile. In Egypt sal-ammoniac was made by burning camels' dung and collecting the sublimate. Putrefied urine (in which the urea has passed into ammonium carbonate) has been used for centuries, and to a certain extent is still used by dyers as a source of ammonia for scouring wool and other purposes. The methodical working up of

urine collected in large quantities, or of sewage for obtaining ammonia therefrom, has been carried out in the neighbourhood of some large towns, *e.g.* Paris, but only a very small quantity of ammonia in comparison with the enormous quantity excreted is actually obtained in this way.

Normal urine contains per litre from 20 to 35 grams urea (carbamide) which after a short time is changed into ammonium carbonate under the influence of a micro-organism. An adult man produces from 22 to 37 grams urea per 24 hours, together with a little uric acid, corresponding to 12.5–21 grams  $\text{NH}_3$  per day, or between 9 and 17 lbs. per annum. If all the ammonia obtainable from London urine were recovered this would amount to 60,000 tons of ammonium sulphate per annum.

In Paris there are daily 2,200 cubic metres (say tons) of urine and night soil taken out of the fosses, and treated by various processes. In the Billange process the sewage is mixed with milk of lime and allowed to settle, the liquid portion is worked for ammonia, the muddy deposit (containing a great many albuminoid matters) is heated by steam, passed through filter-presses and sold as manure. In the Kuentz process the muddy deposit is mixed with a reagent prepared by treating a mixture of bauxite, natural phosphate of lime, and hydrated oxide of iron with hydrochloric acid. The resulting mass is passed through filter-presses; the cakes remaining in these contain all the phosphoric acid (10–12 p.c.) as di-calcic phosphate, precipitated by ammonium carbonates; the iron has absorbed the sulphur compounds, and the alumina has modified the albuminous and slimy matters which would have impeded the filtration. The percentage of nitrogen in these cakes is 3–5.

These processes only apply to ordinary excreta, not to sewage diluted with water from water closets, &c.

Of the large number of recent proposals for treating sewage &c., we here mention a very few.

J. Duncan tries to remove the ammonia from sewage, and the refuse water of sugar-refineries, by distilling it in a vacuum by means of steam at a temperature not exceeding  $30^{\circ}\text{C}$ . (G. Pat. 27,143 and 28,436). A similar principle has been patented by J. Young (E. P. 3,552, 1882). Bolton and Wanklyn (G. P. 17,386) heat urine or other putrefying liquids; the vapour, mixed with air or carbon dioxide, is passed through calcium sulphate, pure or mixed with other salts. The ammonium carbonate is thereby transformed into sulphate, calcium carbonate being formed. When the reaction is finished the mixture is heated, whereupon the inverse reaction is started; the ammonium carbonate which escapes is condensed as usual, and the remaining calcium sulphate is used over again as at first.

Further patents are those of Schneider (G. P. 27,671 and 32,890); Riechers and Hagen (G. P. 14,210); Brüllé and Leclerc (E. P. 1,086, of 1880); Van Ruymbeke (Am. P. 342,237); Buhl and Keller (G. P. 27,671).

Chateau (Bl. 35, 195) describes the apparatus employed at Arcueil for burning the noxious vapours escaping in the treatment of sewage, urine, &c., for the recovery of  $\text{NH}_3$ .

E. *Ammonia from guano &c.*—Whilst the ammonia obtainable from excreta is mostly lost for immediate recovery, as it quickly passes away into the water, the soil, or the air, there are a few exceptions to this rule presented by the deposits of birds' excrements on some desert islands, and a few similar cases. In this 'guano,' ammonia salts exist already preformed, and ammonia can be formed from other nitrogenous substances contained therein by heating guano with lime (as patented by Young in 1811), but this process is not remunerative, since the direct manurial value of guano is much superior to that of the ammonia salts obtainable therefrom.

F. *Bones, horn, leather, and other animal substances* rich in nitrogen yield considerable quantities of ammonia in dry distillation. When manufacturing bone-charcoal (the 'char' of sugar-refiners) it is possible to collect the liquid products of dry distillation, consisting of tar and ammoniacal liquor, and this process is frequently carried out, especially in Great Britain. On the continent it is less usual, as the beet-root sugar-makers prefer charcoal made in pots to that made in closed retorts, but attempts have been made to recover the ammonia in the former case by washing the gases ('scrubbing'), although in this case much of it must be lost owing to the heat being much greater than when employing retorts. It is also very difficult to treat such dilute gases without injuring the draught of the furnace. The treatment of the ammoniacal liquors obtained in manufacturing bone-charcoal, or in the dry distillation of horn, hoofs, hair, leather, &c., as a preparation for the manufacture of prussiate of potash, is exactly like that of the gas-liquor to be described below. They are in the same way obtained in the first instance by means of air-cooled condensers and scrubbers, exactly similar to those used in the manufacture of coal-gas. The remaining gases, which still possess a very disagreeable smell, are conveyed back into the retort fire and are burnt there, care being taken to introduce them in a very hot place, so that the combustion may be complete. The passage of the gases may be promoted by an injector or exhauster. The condensing liquids are separated, by settling, into tarry matters ('Dippel's oil') amounting to 1·7–2 p.c. of the weight of the bones, and hitherto mostly burnt under the retorts, and ammoniacal liquor, yielding from 6 to 7 p.c. of ammonium sulphate on the weight of the bones, of somewhat inferior quality and strongly coloured. Horn, when distilled as a preliminary to the manufacture of prussiate of potash, yields, according to Dumas, 50 p.c. ammoniacal liquor at 8–10° Twaddell and 16 p.c. of Dippel's oil.

Some inventors try to increase the quantity of ammonia, and to destroy a portion of the objectionable organic impurities, by passing the gases over red-hot lime, &c., as H. P. Lorenzen (G. P. 9,989), and H. J. and E. B. Castner (E. P. 4,057, 1882); or by distilling animal refuse matters together with lime (Proschwitzky, G. P. 10,957), or caustic soda (L'Hôte), or carbonate of potash (Th. Richters, G. P. 13,594).

In the last case the residue contains a large

quantity of cyanogen compounds, and can be utilised for manufacturing ferrocyanides.

The most successful treatment of such animal refuse matters which cannot be utilised in other ways, as leather cuttings, &c., seems to be to dissolve them in hot concentrated sulphuric acid (which can be done in cast-iron vessels), utilising that acid for manufacturing superphosphate. In this case most of the nitrogen is converted into ammonia, as is done in Kjeldahl's analytical process for determining nitrogen.

G. *Ammonia formed in inorganic chemical manufactures.*—A very perceptible quantity of ammonia is formed in the manufacture of caustic soda, in oxidising the sulphur compounds by means of sodium nitrate (comp. especially Lunge and Smith, S. C. I. 1883, 460 and 525). Although this ammonia is dispersed in an enormous volume of other gases, it is actually recovered at the Aussig works, where, in 1881, sixty tons of ammonium sulphate were obtained from this source.

L. Tralls (Application for G. P. T. No. 1,860, of January 26, 1887) believes he can obtain ammonia in manufacturing sulphate of alumina from alum-schists, by adding 1 p.c. of calcium sulphate before calcining it.

H. *Ammonia as a by-product in the manufacture of beet-root sugar.*—Ammonia can be got from beet-root juice and from the mother-liquors produced in working it up. During the evaporation of beet-root juice, ammonia is given off, which Vibrans (G. P. 15,513) proposes to collect. Much more can be got by the dry distillation of the 'vinasse,' that is, the liquid remaining behind when beet-root molasses have been made to ferment, and the alcohol has been distilled off. It is probably the betaine, discovered by Scheibler as a constituent of the beet-root, which by its decomposition furnishes both ammonia and trimethylamine. The process proposed in 1878 by C. Vincent (C. N. 39, 107) principally aims at obtaining trimethylamine and methylchloride; but a number of other processes are intended to convert practically the whole of the nitrogenous compounds contained in the vinasse into ammonia. Thus Ernst (G. P. 13,871, 17,869 and 18,549) mixes the concentrated vinasse with lime and fatty oil, and distils the mixture in a retort of peculiar construction. Other apparatus for this purpose are those of Lederer and Gintl (G. P. 17,871), of F. X. Brosche (G. P. 14,433), of the Badische Gesellschaft für Zuckerfabrikation (G. P. 15,702), of Haring, Ehrenberg & Co., and M. Baswitz (G. P. 15,751). From the potash made from vinasse, which contains some cyanides, Legrand and Dabernard (Fr. Pat. Dec. 27, 1876) believe they can obtain 1–4 p.c. of ammonium sulphate by treating it with steam. Other inventors treat the alcohol employed in recovering sugar from molasses, for ammonia, as H. Steffens (G. P. 23,594) and R. Schiller (G. P. 38,596).

If all the beet-root sugar-works in Germany were able to recover the total ammonia given off during the manufacture it would amount to 15,000 tons of sulphate per annum.

I. *Peat* and analogous vegetable matters sometimes yield large quantities of ammonia, either already formed (and probably first ab-



sorbed from the air) or obtainable from nitrogenous organic substances. The nitrogen of organic substances, more particularly that contained in 'Bruchinmoor' and 'Grünlandmoor' (special kinds of peaty moorlands), which amounts to 3·8 p.c., is intended to be recovered in the shape of ammonia by the process of Grouven (G. P. 2,709; 13,718; 18,051; 34,086). The principle of the process is to mix the damp peat with chalk (in order to fix the sulphur), to heat this mixture in upright cylinders by means of the gases remaining from the subsequent stages of the process, and to pass the gaseous products of this dry distillation through a 'contact-substance,' consisting of peat, chalk, and clay in exact proportions, moulded into the shape of drain-tiles and heated in upright cylinders to a proper temperature. Here the nitrogen, under the influence of the incandescent aqueous vapour, hydrogen, and hydrocarbons given off in the first cylinders, is to a great extent converted into ammonium carbonate, which is condensed by calcium sulphate, and thus converted into ammonium sulphate.

Grouven's process has been the subject of prolonged experiments which, however, did not meet with pecuniary success, in spite of the then high price of ammonia. The question of utilising the very large quantity of nitrogen contained in peat is therefore not yet finally solved, although the best descriptions of peat are said to yield up to 8 p.c., and even inferior qualities 4 p.c., of ammonium sulphate.

Leneauchez's 'gazogène distillateur' (described by Cam. Vincent, 'Industrie des produits ammoniacaux,' p. 82) is intended to recover ammonia in employing peat as raw material for gas-producers. This matter should be taken in connection with the processes to be enumerated under L. 6.

K. *Ammonia from bituminous shale* is obtained in the Scotch shale-oil works by washing the gases with water. The quantity of ammonia obtained from this source is very considerable, amounting to 18,000 tons in 1886. The recovery of ammonia in this industry is carried out exactly like that from coal (to be mentioned under L.), and many of the proposals for increasing the yield of ammonia from coal apply equally to shale.

L. *Ammonia from coal*.—There is always a considerable quantity of nitrogen contained in coal, much more than in fresh vegetable matter; in all probability most of this nitrogen is due to the animals which lived during the growth of the coal-forming forests or swamps, and whose remains were buried in them. The same origin is no doubt attributable to most of the nitrogenous substances found in bituminous shales, some of which approach the most shaly varieties of coal so nearly that it is difficult to draw a sharp line of demarcation between them.

The percentage of nitrogen in coal varies from about 1 to 2 p.c. According to Tidy (Lunge's Coal Tar and Ammonia, 541) Welsh coal contains 0·91, that from Lancashire 1·25, from Newcastle 1·32, from Scotland 1·44 p.c. of nitrogen. W. Foster (Proc. Inst. Civ. Eng., 77, pt. iii, 23) found 0·91 p.c. of nitrogen in Welsh anthracite, 1·66–1·75 p.c. in English coal, and 1·28 p.c. in Scotch cannel.

Knublauch (J. für Gasbel. 1883, 410) found in five samples of Westphalian coal 1·215–1·612, in two samples of English coal 1·102–1·443 p.c. of nitrogen. E. Schilling (*ibid.* 1887) has shown that most previous analyses were not quite accurate: his own analyses, made by the Kjeldahl process, yielded on an average for Westphalian coal 1·50, Saar coal 1·06, Silesian coal 1·37, Bohemian coal 1·36, Saxon coal 1·20, Boldon gas coal 1·45, Pilsen cannel-coal 1·49, Bohemian brown-coal 0·52 p.c. of nitrogen. He found on the whole that the percentage of nitrogen in coal decreased with an increase in the percentage of oxygen.

Only a small portion of the nitrogen contained in the coal is utilised. If we take the quantity of coal annually burnt as 400 millions of tons, and its average percentage of nitrogen as 1·33, this would be equal to 5,320,000 tons of nitrogen, or about twenty-six millions of tons of ammonium sulphate—i.e. about 200 times as much as is now obtained from all sources. But it may be safely said that upwards of 90 p.c. of all coal is used in such a manner that a recovery of its nitrogen in the shape of ammonia is practically impossible; of the remaining 10 p.c. only that portion from which coal-gas is manufactured is fully utilised for the production of ammonia, and even here, as we shall see, only a comparatively small portion of the nitrogen is recovered as ammonia. Apart from the question whether there might not be an increase effected in the yield of ammonia in the manufacture of coal-gas, it is beyond all doubt that the quantity of ammonia now in the market might easily be doubled, and more than that, by resorting generally to the recovery of by-products in the manufacture of coke, or by carbonising coal in other ways. This fact should be kept in view when considering the proposals to revolutionise the conditions of burning coal as fuel, by doing this in such a way that tar and ammonia are obtained as by-products.

1. *Production of ammonia in the manufacture of coal-gas*.—In this manufacture it is necessary to purify the gas by subjecting it to cooling ('condensing') and washing ('scrubbing'). In this process an oily and an aqueous substance are obtained, which separate by settling and form *coal-tar* and *gas-liquor*. The latter comes from the hydraulic main, the condensers and scrubbers. The quality of the liquor from these sources is very unequal, that of the condensers being the best, but in most gasworks they are all united. Sometimes that which condenses without washing is collected by itself as 'virgin gas-liquor.' Some liquor always remains incorporated with the tar, and is obtained partly by subsidence and partly by distillation.

A description of the condensers and scrubbers used at gas works will be found in the article COAL-GAS.

Nothing like all the nitrogen contained in the coal distilled is recovered as ammonia; at most a fifth, but sometimes as little as a tenth, is actually obtained as such. From coal with 1·33 p.c. N. we ought to get 6·65 p.c. ammonium sulphate, or 149 lbs. to the ton, whilst 20 lbs. or at most 22 lbs. is considered as a fair yield. In a laboratory experiment, W. Foster (C. S. 43,



105) obtained, of 100 parts of nitrogen contained in coal: 14.50 parts as ammonia, 1.56 as cyanogen, 35.26 in the elementary condition (as part of coal-gas), 48.68 remaining in the coke. Watson Smith (*ibid.* 45, 144) showed that coal-tar must also be taken into account for some nitrogen. In ordinary gas-retort coke he found 1.375, in bee-hive coke 0.511, in Simon-Carvès coke 0.384 p.c. nitrogen, showing that much less nitrogen is driven out in the short process of gas-making than in the long-continued process of coking proper. Cl. Winkler found that in coke-ovens 28.7 p.c. of the nitrogen remained in the coke, 71.3 p.c. escaping with

the gases. Knublauch (J. für Gasbel. 1883, p. 440) found that in gas-making on the large scale, 31–36 p.c. of the nitrogen remained in the gas coke, 10–14 was recovered as ammonia, and 1.5–2 as ferrocyanide, whilst 1.0–1.3 was contained in the tar, and about 50 in the gas. The most trustworthy statements in this direction have been made by E. Schilling (*ibid.* 1887), founded upon accurate experiments with a working gas retort, specially adapted for this purpose, at a temperature of 1160–1220°. A short summary of his results is given in the following table:—

	Description of Coal							
	West-phalian	Boldon gas	Silesian	Bohemian	Saxon	Saar	Bohemian tunnel	Brown coal
Total nitrogen, per cent. . . . .	1.50	1.45	1.37	1.36	1.20	1.05	1.19	0.52
Of 100 parts N left in coke . . . .	80	72	70	69	64	57	44	38
„ „ volatilised . . . . .	20	28	30	31	36	43	56	63
Percentage yield of $\text{NH}_3$ on the coal . .	0.248	0.189	0.284	0.237	0.094	0.188	0.221	0.129
Yield of N as $\text{NH}_3$ on the total N per cent. . . . .	13.6	10.8	17.4	14.2	6.4	14.8	18.4	20.7
Yield of ammonium sulphate (lbs.) per ton of coal . . . . .	22.3	17.0	25.6	21.4	8.5	16.9	19.9	11.0

An increase of the yield of ammonia in gas-making is aimed at by the following processes:—

A. Cooper's lime-process.—W. J. Cooper (E.P. 5,713, 1832; comp. Wanklyn, S. C. I. 1883, 438; 1884, 12) mixes  $2\frac{1}{2}$  p.c. lime of the weight of the coal, previously slaked to a powder, with the coal before charging it into the retorts. This produces a substantial gain of ammonia, and a much smaller percentage of sulphur in the gas. The latter is a doubtful advantage, since the sulphur retained in the spent oxide is valuable, while that retained in the 'limed' coke is just the contrary. In England the highest yield of ammonia by this process was 36lbs. of ammonium sulphate per ton of coal. Schilling (*loc.*) found that in the case of Boldon coal there was an increase of 30.7 p.c. of ammonia by 'liming' the coal, but in the other cases only a slight increase (3–11 p.c.), or even a slight decrease (2–4 p.c.); only the exceptionally poor yield from Saxon coal was very greatly increased (84 p.c.). Knublauch (J. für. Gasb.) found 20 p.c. more ammonia, and 5 p.c. more but poorer gas; there was a falling off in the quantity (10 p.c.) and in the quality of the tar. There seems to be no great prospect of this process being generally adopted.

B. Tervet's process (E. P. 1872, 1883) of passing hydrogen over coal, shale, &c., in the retorts yielded very good results on a minute laboratory scale, but much less good results on a slightly larger scale. It seems never to have passed the laboratory at all.

C. Injection of steam has been frequently proposed, but this seems hardly practicable for real illuminating gas (*v.* below).

The direct recovery of ammonia from illuminating gas in the shape of a compound suitable as a fertiliser, without the intervention of producing ammoniacal liquor and without having to distil the ammonia from this, is effected by

the process of Bolton and Wanklyn (G. P. 16,788). They pass the gas, previously freed from tar, through a purifier charged with superphosphate, where the ammonia is to be retained by the free acid or the monocalcium phosphate; the resulting ammoniacal superphosphate is to be sold as a manure. This process has been tried at the Munich gas-works (Bunte, Fischer's Jahresber. 1882, 281); according to the conditions of working from 8.5 to 31 p.c. of the total ammonia was thus recovered in the superphosphate, but it must be considered that part of this consists of sulphocyanide which is supposed to be injurious to vegetation; also that the soluble phosphate is thereby transformed into precipitated phosphate. The latest reports on this process (J. für Gasbel. 1887, 1,061) are very favourable to it.

The spent oxide from the gas-purifiers also contains considerable quantities of ammonia. This can be recovered by lixiviation, either hot or cold. Richters (G. P. 15,206) combines the revivification of spent oxide with the recovery of ammonia, by passing air through the mass, contained in close boxes; the heat produced in the oxidation of the ferric sulphide drives off the ammonia.

2. Some modern processes are intended to make the production of ammonia a principal feature in the treatment of coal or shale, and to obtain the heating value of the latter as a secondary product, mostly in the shape of 'water-gas.' It has long been known that the injection of steam when carbonising nitrogenous organic substances increases the quantity of ammonia obtainable therefrom, and the process of H. Grouven, mentioned above, which dates as early as 1878, takes advantage of this fact for utilising the nitrogen of otherwise useless descriptions of peat. But when applying this process to bituminous shale or to coal, it must be noted

that a sensibly increased yield of ammonia can only be obtained by applying a considerable quantity of steam, and that, at the same time, the conditions for producing an increased yield of ammonia and those for producing 'water-gas' of good quality, corresponding to the reaction  $C + H_2O = CO + H_2$ , are opposed to each other, as we shall see directly. It is, therefore, unlikely that the recommendations made by W. Foster (Proc. Inst. Civ. Eng. 1833-84, v. 77, pt. iii.) will have any practical success, especially as his calculations concerning the thermal value of water gas have been shown to be quite erroneous (comp. *ib.* 65 and 76), and as, even with the improvements made by Young and Beilby (comp. below) the reaction taking place in this instance yields far more  $CO_2$  than  $CO$ .

Several attempts had already been made in this direction, e.g. by W. Young (E. P. April 12, 1881); G. Beilby (E. P. May 18, 1881); W. Young and G. Beilby (E. P. March 21, 1882). Young and Beilby recover part of the nitrogen contained in bituminous shale and coal by burning them in the presence of steam. Their process is described at length by Beilby (S. C. I. 1884, 216). He found that of 100 parts of the nitrogen contained in bituminous shales (amounting to about 1 p.c.) there is recovered on distilling them in the usual manner for the production of paraffin-oils: 17.0 as ammonia in the watery distillate, 20.4 as alkaloidal tar, 62.6 in the residual coke. When the distillation was carried on first at a low red heat, and the residue was afterwards subjected to a bright red heat in the presence of steam, only 4.9 nitrogen was left in the coke, 74.3 being recovered as ammonia and 20.4 as nitrogenous tar. A certain proportion of air may be mixed with the steam, without seriously reducing the yield of ammonia. This has the advantage that a certain amount of heat is generated within the retort, and less heat has to be supplied from the outside.

The theoretical problem to be solved is that of applying steam in such a way that the carbon is utilised as 'water-gas,' by the reaction  $C + H_2O = CO + H_2$ , whilst the nitrogen, also, by the action of steam, is caused to pass for the most part into ammonia. Unfortunately the temperature at which carbon freely decomposes water is considerably above that at which ammonia is decomposed; the former may be taken as  $1100^\circ$  to  $1200^\circ$ , whilst according to Ramsay and Young (C. J. 1884, 88) the decomposition of ammonia in favourable circumstances commences rather below  $500^\circ$  and is nearly complete at  $780^\circ$ . This difficulty can be avoided only by diluting the ammonia gas with a large quantity of neutral gas. Grouven effects this for analytical purposes by passing a quantity of steam through the apparatus equal to 20 or 30 times the weight of the substance. This is evidently impossible to apply on an industrial scale, but Young and Beilby have found that, by mixing steam and air, 60 to 70 p.c. of the nitrogen can be obtained as ammonia on a large scale with an expenditure of only  $1\frac{1}{2}$  parts of steam to 1 part of coal. The heating gas obtained at the same time, that is, even with Young and Beilby's improvements, was certainly of a poor description, viz. containing in 100 parts by volume 16.6  $CO_2$ , 8.1  $CO$ ,

2.3  $CH_4$ , 28.6 H, 44.4 N, and it is hence doubtful whether this process will pay in actual practice, especially as it involves the erection of costly plant. The different retorts or furnaces constructed for this purpose are described and illustrated in the memoir quoted. They consist essentially in vertical shafts, in the upper half of which small coal is carbonised, the coke descending into the lower half, where it is burned with air and steam: the gases and vapours generated in the upper portion are passed through the red-hot coke contained below, and are here completely converted into permanent gases and ammonia. The cooling and condensation is effected in large brick chambers where water is injected in fine jets of spray crossing each other; as the velocity of the gases is very slight, the cooling and washing processes should be very thorough.

L. Mond (E. P. 3,923, 1883; 8,973, 1885) applies a similar principle to *gas-producers*, in which a low temperature and an excess of steam is conducive to the formation of ammonia. He describes special means for condensing tar and ammonia. This process has been carried out on a working scale with good success; it yields a very considerable quantity of ammonia, but much poorer gas than the ordinary process, and it must depend upon the relative value of ammonia and coal whether there is a profit in it or otherwise. It appears that it is going to be carried out on a very large scale.

We shall further quote the patents of G. R. Hislop (5,252, 1882); of H. Simon and Watson Smith (4,871, 1883); of H. Kenyon (1,016, 1886); of A. French (5,945, 1885).

3. *Ammonia from coke-ovens*.—Whilst in the manufacture of coal-gas the ammonia evolved has been collected ever since the commencement of this industry (as witnessed by the patents of Lord Dundonald in 1781, of Winzler or Wiusor, in 1804 and the following years, &c.), owing to the fact that it was necessary for the purification of the gas, on the other hand the ammonia produced in the consumption of coal for *coke-making in blast-furnaces* and for all other purposes has been wasted until a very recent period. During the last few years, however, the problem of more fully recovering the nitrogen of coal in the shape of ammonia has received a very great amount of attention.

According to Gurlt the earliest attempt to collect tar and ammonia from *coke-ovens* was made by Stauf in 1764, at an ironworks near Saarbrücken. The first really successful apparatus of this kind was constructed by Carl Knab at St. Denis, in 1856. His ovens were originally only provided with bottom-flues; on introducing Knab's ovens at Commeny, Carvès (1862) added side-flues, and these improved ovens were introduced in 1866 at the Bessèges iron-works, and 1879 at Terre-Noire. About 1870 the coke-ovens known as those of Pauwels-Dubochet were arranged on a similar plan, but they do not seem to have had the same effect as far as the quality of the tar is concerned; about the ammonia nothing is said (Watson Smith, S. C. I. 1884, 603). The Carvès oven has been further improved in 1882 by H. Simon, of Manchester, who added a previous heating of the air to  $500$ – $600^\circ$  by means of the waste heat

of the fire-gases. Some earlier efforts at saving tar and ammonia in coking are mentioned by Watson Smith.

The apparatus devised for recovering ammonia (and tar) as by-products in coking may be classed as follows:—

I. Those which are merely a modification of the ordinary coke-oven, where the heating is effected by admitting air and thus burning part of the coal to be coked. The best-known examples for this are Jameson's, comp. S. C. I. 1883, 114 (G. P. 27,694, 24,915 and 25,676, E. P. 14,551, 1885) and Lürmann's coke-oven (G. P. 17,203). In the Jameson coke-oven the quantity of ammonia obtained is not worth the collecting, as stated by the inventor himself (J. Soc. Ch. I. 1885, 314). Lürmann's ovens have also proved a failure. Probably the temperature in this kind of furnace is too high for the production of considerable quantities of  $\text{NH}_3$ .

II. Those where no air is admitted into the interior of the coke-oven, all the heating being done from the outside by means of the gas escaping from the coal in the coking process, after taking the tar and ammonia out of it. Nearly all the modern coke-ovens belong to this class, of which it is impossible to describe all the modifications. Those invented within the last few years have been described in the S. C. I. 1883, 322; 1884, 601; 1885, 112 and 484. For a synopsis of the whole field up to the middle of 1887, we refer to Lunge's *Coal Tar and Ammonia*, p. 38-82 and 711-715. Over and above the 'Hoffmann-Otto' and the 'Simon-Carvès' ovens, principally treated there, we must now quote the excellent type of coke-ovens, invented by Th. Bauer (the original inventor of the 'Hoffmann' coke-oven), as patented from 1884 onwards (G. P. 28,530, 32,235, 32,660).

Without going into any details of construction we will in a few words describe the general principle followed in every one of those really successful modern coke-ovens. They are all constructed (with an infinite variety of detail) on the principle of a close chamber, practically a very large retort, from which the gases evolve in the distillation of the coal are mechanically aspirated without any admixture of air or fire-gases. The gases pass through condensers, cooled on the outside by air or water, where they deposit a great deal of their tar and ammonia; the remainder is taken out by scrubbers, and the residual gas is then carried back to flues surrounding the coking-chambers, in order to be inflated by means of a current of (previously heated) air, and to heat the coking-chambers from the outside. After having effected this purpose, the waste fire-gases are employed for the previous heating of the air, serving for combustion in 'recuperators' of various descriptions. By this process the following advantages are realised. Whilst in the ordinary coke-making process no tar or ammonia is obtained, the new process produces, from ordinary coking-coal, about 2-3 p.c. of excellent tar and about 1 p.c. of sulphate of ammonia; it also leaves a considerable amount of gas at disposal for heating steam-boilers, &c.; last, not least, it increases the yield of coke from 60 to about 70 or 75 p.c. of the coal—that is, about one-fifth to one-fourth. The quality of the coke, as obtained in

the best new ovens, is fully equal for all smelting purposes to the best bee-hive coke, notwithstanding the prejudice of many ironmasters against it. The only real drawback to the new process is the large amount of capital required for the plant, but this is tending to be greatly reduced now—e.g. in the Bauer ovens.

4. *Ammonia from blast furnace gases* can, of course, only be obtained in the case of blast-furnaces fed with raw coal, as is done in Scotland. We refer here also to the descriptions in Lunge's *Coal Tar and Ammonia*, pp. 85-90 and 557-563. One of the most successful of these processes is that of Alexander and McCosh (E. P. 4,117, 1879; 1,433, 1880; 3,785, 1881). This process has been carried out at the Gartsherrie ironworks. The gas escaping from the blast-furnace mouth is carried through an arrangement of pipes alternately communicating at top and bottom, where the cooling action of the air can set in. The bottom communication consists in a trough with suitable divisions, where the condensed ammoniacal liquor and tar collects. The whole apparatus is exactly like that used in ordinary gas-works. It is followed by a set of scrubbers, not filled with coke, like ordinary gas-scrubbers, but provided with a number of perforated shelves, which leave room for the passage of the gas alternately at opposite sides, whilst water is continually trickling down through the perforations and washes out the ammonia still contained in the gas. The liquid collecting at the bottom is pumped up again and used over again till it is sufficiently saturated with ammonia. The gas, after being freed from tar and ammonia, is utilised for heating purposes, like ordinary blast-furnace gases.

The process of Alexander and McCosh is substantially identical with that of W. S. Sutherland for recovering tar and ammonia from producer-gases (S. C. I. 1883, 459). The Dempster and the Henderson process are also very similar.

The quantity of ammonium sulphate obtained from blast-furnace gases at the Gartsherrie ironworks is about 0.9 p.c., latterly up to 1.36 p.c. of the weight of coal passing through the furnace (together with 10.2 p.c. of tar). This is equal to the quantity of ammonia obtained by the Carvès process, although the volume of the gases to be treated in the blast-furnace is thirteen times that of the gases evolved when previously coking the coal by itself (J. L. Bell, *Engineering*, 37, 378). This evidently involves an immense amount of cooling and compromises the economical working of the process. This drawback is intended to be avoided by the process of Addie (E. P. 4,758, 1882 and 3,246, 1883), which is also applicable to the gases from coke-ovens and gas producers. They are mixed with sulphur dioxide, sufficient to fix the ammonia as sulphite, and are then passed through a scrubber where the sulphite is dissolved out and the resulting solution is oxidised into sulphate by injecting air into it, or else it is distilled with lime and the ammonia utilised in the usual manner. The liquors actually obtained by this process contain sulphate, sulphite, and thiosulphate in varying proportions (S. C. I. 1883, 458).

Similar processes had been previously applied to ordinary coal-gas by R. Laming and by W. Huns (1852), and latterly to producer-gas by



G. E. Davis (S. C. I. 1883, 521). The Société de Hüssigny (Lake's E. P. 5,898, 1884) absorbs the ammonia from furnace gases by calcium chloride. A very complete paper on the whole subject has been read by W. Jones at the Iron and Steel Institute's meeting in Glasgow in 1885 (abstr. S. C. I. 1885, 737). He states that, if all the blast-furnace gases in Scotland were treated for the recovery of ammonia, the yield of ammonium sulphate would be some 18,000 tons per annum, equal to 22 p.c. of the present production of Great Britain.

5. A number of German patents taken out in 1883 (by Neumayer, Lorenz, Wellstein), treat of the recovery of ammonia from hot furnace gases of all descriptions by means of injecting into them heated acid in a fine jet.

6. Very many attempts have recently been made to recover the ammonia from the gases of gas-producers or generators. These processes generally resemble those applied to coke-oven and blast-furnace gases, and, like these, mainly consist in cooling and scrubbing the gas, exactly as in the purification of ordinary coal-gas; some of them add to it the action of acids, as just mentioned. There are also some special plans—e.g. the following. F. Siemens (E. P. 9,103, 1885) separates the zone where hydrocarbons are cooled, along with ammonia, from that where the conversion of carbon into carbon monoxide takes place, by a special construction of the gas-producer, in order to more easily condense tar and ammonia.

T. B. Fogarty (Lake's E. P. 5,361, 1883) passes producer-gas, raised to a very high temperature through a shower of finely comminuted carbon and alkali, which combine with some of its nitrogen to form cyanide. This in its downward course is decomposed by steam, ammonia being formed, which is recovered by a scrubber.

One of the principal attempts in this direction is the process of Mond, already mentioned (v. No. 2), in which the quality of the gas is sacrificed to the greatly increased yield of ammonia.

We must further mention the process of G. H. Davis (E. P. 5,717, 1882; 4,468, 1883; S. C. I. 1883, 522), which principally aims at very greatly increasing the quantity of benzol

by distilling coal at a very low temperature, say about 650°C. He thus obtains from 1 ton of coal 37 gallons of ammoniacal water, together with 16 gallons of tar, 4 gallons of 90 p.c. benzol from the gas, and a residual gas well adapted for heating purposes. There seem to be several 'carbonising works' in England which treat the gas produced in the distillation of coal as a by-product, tar and ammonia being the principal products. These works can evidently only be carried on when tar and ammonia command a fairly good price, which has sometimes not been the case lately.

The following official statement of the amount of ammonium sulphate produced in 1886 (Twenty-third Annual Report on Alkali &c. Works, 26), proves that so far the greatest portion of ammonia still comes from gas-works, the only considerable competitors having been the Scotch shale-works:

Gas-works . . . .	82,480 tons
Iron-works . . . .	3,950 "
Shale-works . . . .	18,080 "
Coke and carbonising works.	2,100 "

Total for the United

Kingdom . . . . 106,610 "

## II. The working up of ammoniacal liquor.—

The ammoniacal liquor from the manufacture of coal gas (to which the liquors obtained in other manufactures bear great resemblance in all essential points) is a liquid of a colour varying from light yellow to dark brown, of an ammoniacal and at the same time fetid smell. Its principal constituents, apart from small quantities of tarry, ill-defined substances, some of them phenols, are ammonium salts: carbonate and sulphide (which always prevail), sulphocyanide, ferrocyanide, chloride, sulphate, thio-sulphate, sometimes sulphite, perhaps also free ammonia. Together with these occur the salts of organic nitrogenous bases. The proportions in which those salts are distributed vary greatly, both according to the nature of the coals distilled and the way in which the distillation had been carried on. The following table, by Gerlaech, gives an idea of this, but it cannot be exact, since no sulphocyanide is mentioned:—

One litre of gas-liquor contains in grams:

	Chemnitz works, Zwickau coal	Saxon town, Zwickau coal	Bonn works, Ruhr coal	Treves works, Saar coal	Zürich, Saar coal
Total ammonia . . .	12.090	9.40	18.12	15.23	3.47
Ammonium thiosulphate . .	1.036	1.628	5.032	2.072	0.296
" sulphide . . .	0.340	0.646	5.222	2.468	1.428
" bicarbonate . . .	1.050	1.470	2.450		
" monocarbonate . . .	4.550	7.580	33.120	33.763	5.856
" sulphate . . .	0.462	0.858	1.320	4.922	1.925
" chloride . . .	30.495	17.120	3.745		
Salts, total . . .	37.943	29.402	51.889	43.225	9.506

The valuation of gas-liquors is, at least in Great Britain, frequently if not generally performed at the gas-works by means of the hydrometer. This method is, however, most deceptive, for the ammonium salts raise the density of the liquor in an unequal degree, and free ammonia (which, however, does not seem to occur frequently) even lowers it. It is hence de-

cidedly preferable to value gas-liquor by a chemical test. In England it is usual to prepare a standard acid by diluting 1 lb. of rectified oil of vitriol to a gallon; the dilute acid ought to be of sp. gr. 1.068. 16 liquid ounces of the gas-liquor are measured off and the acid is run in from a measure graduated to liquid ounces, till litmus paper indicates neutrality. (A solution of litmus

cannot be employed, both on account of the original colour of the gas-liquor and of the H<sub>2</sub>S evolved). The number of the measures of acid consumed indicates the number of ounces of concentrated oil of vitriol which each gallon of the gas-liquor requires for saturation. It is generally assumed that each degree of Twaddell's hydrometer corresponds with about 2 ounces of sulphuric acid, *e.g.* gas-liquor of 4°Tw. ought to saturate 8 ounces of acid. But this is anything but correct: usually less acid is required than, according to the hydrometer, should be expected.

If the test-acid is correctly made to contain 100 grams of H<sub>2</sub>SO<sub>4</sub> per litre, each ounce used in the test is equal to 9·3459 ounces of NH<sub>3</sub> per gallon, or 0·217 part NH<sub>3</sub> by weight per 100 parts liquor by volume.

This 'saturation test' only indicates the ammonia combined with CO<sub>2</sub> and H<sub>2</sub>S, but not that combined with other acids. The total ammonia is estimated by the distillation test. A sample of the gas-liquor is distilled with caustic soda, magnesia, or lime, and the vapours

are received into water or at once into standard acid, the unsaturated acid being afterwards determined by standard alkali. S. Dyson, who has given a complete set of methods for the total analysis of gas liquor (S. C. I. 1883, 229) recommends employing magnesia in lieu of soda or lime, because the former is supposed not to set free volatile organic bases, but Lunge has shown (*ib.* 514) that this is a mistake, and that magnesia has the drawback of requiring longer time and a greater excess to act. It seems preferable to use lime, because this is the agent employed on a manufacturing scale, and it is required to know how much ammonia will be obtained by it. The liquid should be distilled almost to dryness, so as to make sure of driving off all the ammonia.

The following tables are constructed from the materials supplied in a paper by J. H. Cox (Journal of Gaslighting, 1883), but the thio-sulphate is not, as there, included in the volatile salts, since this salt on boiling does not decompose any more than the chloride.

I.—Table showing the properties and composition of eight samples of gas-liquor, obtained from the same coal, but taken from different points in the condensing and scrubbing plant.

	Condensed in the hydraulic main	Another point of the hydraulic main	Liquor					
			From first condenser column	From second condenser column	From third condenser column	From fourth condenser column	From first washer	From finishing washer
Colour . . .	very dull orange, turned black in air	very dull orange, turned black in air	colourless	almost colourless	brown red, from light tar-oils	dark brown, from tar-oils	colourless	colourless
Sp. gr. in deg. Tw. at 15·5°C.	2½	2½	7	15	23	24	4½	2
Ounces by distillation test . . .	6·1	6·0	16·2	36·1	53·0	58·0	16·5	8·3
Ounces by saturation test . . .	2·7	2·8	15·9	35·7	52·5	57·4	16·1	8·1
Am. sulphide, grs. per gal.	361	410	243	500	700 NH <sub>4</sub>	810	1·92	1220
= NH <sub>3</sub> , gr. per gal.	182	220	1215	2500		4220	796	610
Am. carbonate, gr. per gal.	561	510	33·4	8120		12,126	4·12	1690
= NH <sub>3</sub> , gr. per gal.	290	81	1200	2830		4300	1600	600
Am. thio-sulphate, gr. per gal.	122	82	trace	125	372	765	230	135
= NH <sub>3</sub> , gr. per gal.	28	19	trace	41	81	176	51	31
Am. sulphate, gr. per gal.	8	34	—	—	—	—	—	—
= NH <sub>3</sub> , gr. per gal.	2	9	—	—	—	—	—	—
Am. thiocyanate, gr. per gal.	112	120	91	trace	—	—	112	27
= NH <sub>3</sub> , gr. per gal.	25	29	2	trace	—	—	25	6
Am. chloride, gr. per gal.	1552	1155	11	155	2·1	107	88	38
= NH <sub>3</sub> , gr. per gal.	493	462	38	50	64	34	28	12
Am. ferrocyanide, gr. per gal.	—	trace	22	41	125	375	—	—
= NH <sub>3</sub> , gr. per gal.	—	—	5	10	30	90	—	—
Total ammonia, gr. per gal.	970	920	2160	5480	8080	8820	2500	1260
Percentage of fixed am. in the total am.	59%	56%	1·8%	1·85%	2·2%	3·1%	4·2%	4·0%
Am. expressed as cwt. of sulphate, per 1000 gallons	4·5	4·5	11·9	26·6	39·3	42·8	11·8	6·1
Value of liquor for sulphate making	very small	very small	very good	very good	excellent	excellent	very good	not quite strong enough

II.—Table showing the properties and composition of various samples of liquor from different coals, and from different points in the condensing and scrubbing plant.

	Condensed liquor passed through scrubber	Another sample taken at different time	Same liquor exposed to air, high temperature	Hydraulic main liquor	Part condenser liquor, part hydraulic main	From 'standard' washer before purifiers
C. lour	yellow	yellow	bright orange	dark yellow	yellow	colourless
Sp. gr. in deg. Twaddell at 15.5° C.	4.5	4	3.5	2	3	4.5
Ounces by distillation test	10.00	8.25	6.9	5.60	6.60	10.00
saturation test	8.30	7.0	4.25	3.10	4.90	10.00
Am. sulphide, grams per gallon	960	1216	630	576	220	1180
" " = NH <sub>3</sub> " "	480	6.8	315	288	110	590
" " carbonate " "	2020	11.5	8.0	—	1692	2540
" " = NH <sub>3</sub> " "	720	410	283.5	193	600	900
" " thio-sulphate " "	195	182	256	—	174	trace
" " = NH <sub>3</sub> " "	45	42	52.5	35	40	—
" " sulphate " "	—	trace	39	—	9	—
" " = NH <sub>3</sub> " "	—	—	10.5	6	2.5	—
" " thiocyanate " "	338	243	472	—	90	—
" " = NH <sub>3</sub> " "	75	54	105	56	20	—
" " chloride " "	567	403	891	—	693	3?
" " = NH <sub>3</sub> " "	180	1.8	283.5	301	220	10.1
" " ferrocyanide " "	trace	—	—	—	31	—
" " NH <sub>3</sub> " "	—	—	—	—	7.5	—
Total ammonia	1500	1250	1050	860	1000	1500
Percentage of fixed ammonia	20	18.3	43	44	29	0.7
Am. expressed as cwt. sulphate per 1000 gallons	7.25	6.00	5.00	4.10	4.85	7.30
Value of liquor for sulphate making	not good	poor	very poor	{ not worth working }	—	very good

Detailed analyses of gas-liquor, obtained under different conditions, are given by L. T. Wright (S. C. I. 1886, 655), *v. also* GAS, COAL.

The working up of the gas-liquor, so far as it was not run to waste, formerly consisted in saturating it directly with sulphuric or hydrochloric acid and evaporating till the sulphate or chloride crystallised out. This caused great nuisance by the gases which escaped on saturation, and the resulting salt was so much discoloured by tarry substances that it would, nowadays, be hardly saleable. Moreover, the evaporation of such dilute solutions takes more fuel than driving off the ammonia from gas-liquor in properly constructed apparatus. This process, now universally preferred, seems to have been first carried out by Watson in 1838.

The apparatus for distilling gas-liquor must be so arranged that it admits of driving off the total ammonia along with as little water as possible, and with a minimum of fuel. It should, therefore, be constructed upon similar principles to that for rectifying spirit of wine, which, as a matter of fact, has served as a model in this case. There are, however, some questions to be considered previously to entering upon the matter of stills themselves.

The first question is this: whether lime is to be used in the distillation or not. In the latter case only the carbonate and sulphide of ammonium are driven off (in a state of dissociation) while the chloride, sulphate, and sulphocyanide remain behind. These fixed salts are decomposed by lime, and their NH<sub>3</sub> is thus recovered, but many, especially British manufacturers, prefer avoiding this complication, as they consider that the ammonia recovered thereby does not pay for the extra trouble and expense. On the continent it is far more usual to employ lime, but only after expelling the volatile salts: this saves time and inconvenience. The escape of H<sub>2</sub>S cannot be avoided even by a great excess of lime as CaS is partly decomposed in the boiling.

It is a further question what kind of heating is most advantageous for distilling ammonia. From experiments made on a manufacturing scale by Dr. Tidy, it would seem that heating by steam directly blown into the liquid is superior to indirectly heating by a steam coil or by a fire from without; in the first case 98.5, in the second case only 92, in the third 90 per cent. of the total ammonia was expelled.

In any case it would be inexpedient to expel the ammonia by heating without utilising the (sensible and latent) heat of the vapours for a preliminary heating of fresh gas-liquor; when doing this, the ammonia is at the same time freed from aqueous vapour by dephlegmation, and a very great saving of fuel is the consequence.

The distilling apparatus must differ according to whether it is the aim of the operation to obtain *liquor ammoniac*, or to receive the vapours in sulphuric acid and to manufacture commercial sulphate of ammonia; or to condense the carbonate and sulphide as a concentrated solution whereby a saving in the cost of carriage, as compared with that of crude gas-liquor, is effected.

The principle of dephlegmation and rectification can be carried out in many different ways, of which we shall here describe some of those most frequently in use in ammonia works.

Many English ammonia works use a Coffey still (first employed by Newton in 1841, fig. 1). This consists of an oblong vessel *b*, and two superposed columns, *c* and *d*, made of wood lined with lead. The bottom vessel is divided into two chambers *b'* and *b''* by a horizontal diaphragm *d*, perforated with many holes. Steam is blown into the bottom compartment and carries away the last traces of ammonia from the liquor which has made its way thereto.



The mixed steam and ammonia then pass through the first of the superposed columns, the 'analyser' *cdef*, which is divided into twelve chambers *fff*, by horizontal diaphragms *gh*, perforated with many holes, and also provided

with a number of valves *oo*, opening upwards, and overflow pipes *p*, seated at the bottom of the next lower compartment, by a 'hydraulic lute.' From there the vapours pass on to the rectifying column *gmh*, filled with similar diaphragms, but

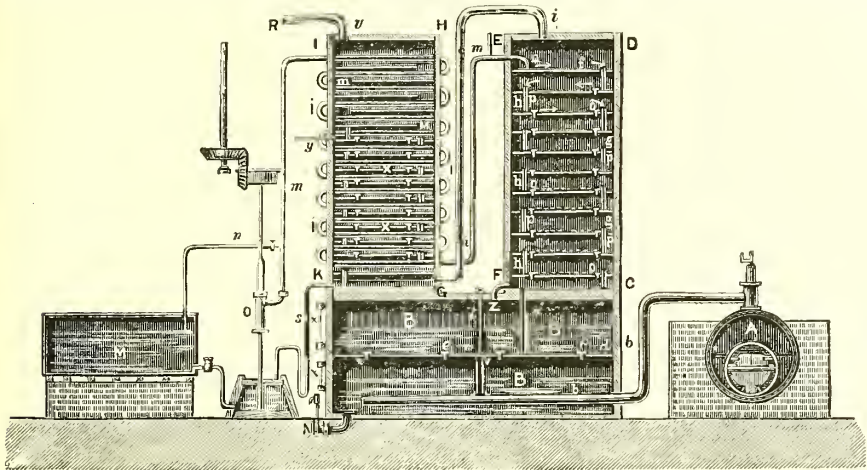


FIG. 1.

containing, moreover, a pipe *m*, which runs in a zigzag course through all the chambers of the rectifier and outside of it rises up again, finally ending near the top of the analyser. Through this pipe gas-liquor is pumped so that

it must run within the pipe through all the chambers of the rectifier, and issues near the top of the analyser in order to flow down through all its chambers, forming a layer on each of the diaphragms, according to the height

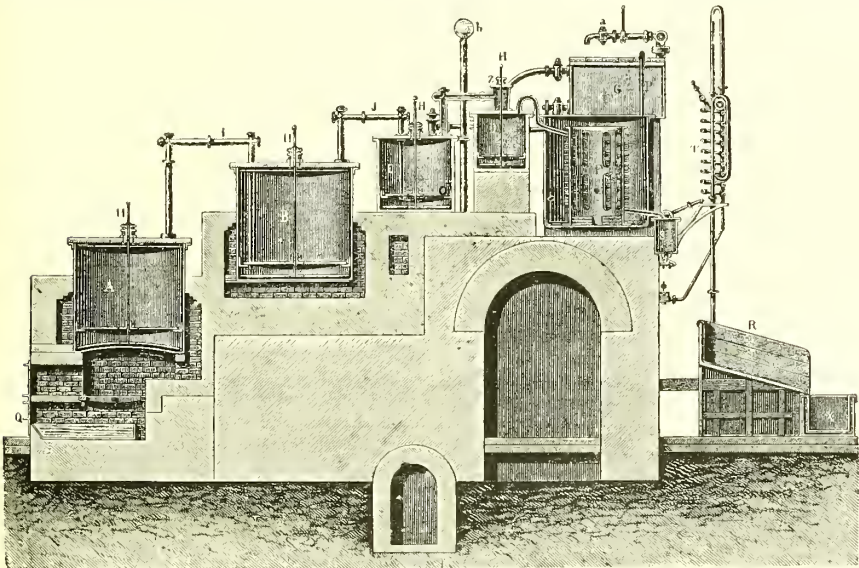


FIG. 2.

of the overflow pipes (the steam meeting it preventing the liquor from flowing through the holes in the diaphragms). Ultimately the liquor reaches the bottom compartment where steam is injected into it. As this passes on through the analyser, it carries off most of the ammonia

contained in the descending liquor, so that but little remains to be driven out in the bottom compartment. The mixture of steam and ammonia, as it passes on through the rectifier, heats the liquor running down in the zigzag pipes almost to the boiling point, but in doing so most

of the steam is condensed, so that almost pure ammonia issues at the top and can either be condensed into a concentrated solution or passed into sulphuric acid to be absorbed. In this way the heat originally supplied by the steam is completely utilised, as is shown by the ammonia passing out almost cool.

This apparatus (as well as Solvay's and several others), rationally as it is constructed, is not very well adapted for distilling gas-liquor with lime, and in fact is used only by those distillers who dispense with lime. Where lime is used, other apparatus is preferred, of which we only describe a few examples.

Mallet's apparatus (fig. 2), principally used in France, consists of a number of upright cylindrical stills, holding above 1,000 gallons apiece, and disposed terrace-wise. The lowest stills, *A* and *B*, are heated by a direct fire; these are provided with mechanical agitating

gear *H*, for mixing the liquor with lime and preventing any burning on. The third and fourth stills, *C* and *D*, serve for washing the vapours from *B*, and are at the same time heated by these. From *D* the vapours enter a worm *F*, 70 or 80 feet long, placed in a tank where it is cooled by gas-liquor. The liquid here condensed flows into a collector, whence it can be emptied back into *D*; the gases pass on through another worm *T*, cooled by air, and ultimately into the vessel where they are to be absorbed. The gas-liquor, which, as we have seen, is to be fed into the outer space of the cooling tank *F*, there undergoes a preliminary heating and then gradually passes on through the stills *D*, *C*, *B*, and *A*, being on its way mixed with lime; the spent liquor is ultimately run out of *A*.

Grüneberg's apparatus, one of those most widely employed, has been modified from time

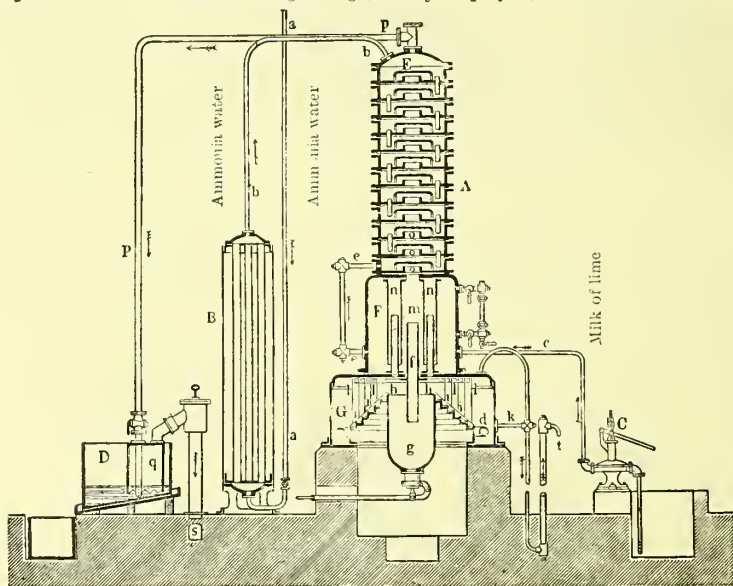


FIG. 3.

to time (G. P. 35, 9,392, 33,320). The apparatus first constructed was heated by a direct fire, the last is intended for heating by steam injected into the liquid. All his apparatuses are intended to work so that the volatile salts are driven off first by the vapours given off by the hotter parts of the liquid; the liquor then arrives at a place where it meets with milk of lime in order to decompose its fixed ammonium salts; and this passage is so prolonged that the spent liquor can be made to run away in a continuous stream, whilst the spent lime is from time to time withdrawn by a sort of valve. The apparatus intended for direct firing is so constructed that the lime cannot form hard crusts on surfaces exposed to the heat of the fire. The fire is applied to the outside of an upright cylindrical still or boiler, which has within it a vertical cylindrical tube, extending below the bottom of the boiler, beyond the heating zone, and there closed with a blow-off

cock or valve. The upper end of this tube reaches nearly up to the top of the boiler and is open to the vapour space of the latter. Above the boiler is a vessel charged with milk of lime from a tank above, and this vessel is again surmounted by a rectifying column, of the description generally employed in spirit stills. The vapours generated in the bottom boiler pass through pipes reaching down near the bottom of the lime vessel into the latter, and keep its contents continuously agitated; they then pass through the successive compartments of the rectifying column. In this the descending gas-liquor is gradually heated and deprived of its volatile ingredients, whilst the ascending vapours are partly condensed and mix with the descending liquor; the uncondensed gases, together with those liberated from the descending liquor, pass away through a pipe into the vessel or worm, where they are to be absorbed in water or sulphuric acid. From the bottom of the column the

liquor, still containing the non-volatile ammonium salts, flows into the lime-vessel and is there mixed with its contents. The whole descends through an overflow pipe into the bottom of the central tube of the bottom boiler, where the lime is deposited, so that it does not come into contact with the heated outer surface of the boiler; only the clear liquor, gradually rising in the central tube and from this overflowing into the outer space of the boiler, is exposed to the action of the fire, and is thus deprived of the last traces of ammonia, a large quantity of steam being generated at the same time, which passes through all the parts of the apparatus previously mentioned, and there acts as described. From the bottom of the boiler the spent liquor rises again in a tube and overflows through a deep hydraulic seal as fast as liquor descends from above.

A new modification, patented by Grüneberg and Blum (G. P. 33,320) is preferable in all cases where there is steam at disposal. Fig. 3 shows this apparatus as adapted to the manufacture of ammonium sulphate. *a* is the still, *b* the gas-liquor heater (economiser), *c* the lime-pump, and *d* the saturator. The gas-liquor enters the heat economiser *b* by means of pipe *a*, and flows from this by pipe *b* into the column *e*, which serves to drive out the volatile ammonium salts. The lime vessel *f*, into which milk of lime is pumped by means of pump *c* and pipe *c*, serves to expel the fixed ammonia, and the boiler *g*, with its stepped cone, serves to boil the liquor in thin sheets, by means of the steam coil *d*, and thus to set free the last portions of ammonia. In *b* the first heating of the liquor takes place by means of the hot vapours from the saturator *d*, which ascend through the bell *g*, the pipe *s* and the inner pipes of *b*, while the liquor, arriving at *a*, rises up in *e*. It then enters through *b* into the dephlegmating column *e*, and finds its way downward from chamber to chamber, till it gets into the lime-vessel *f*. From here it overflows by pipe *f* into the sludge-catcher *g*, overflows here again all round at *h* and runs over the cone *i* downwards from step to step; from the pipe *k* it is discharged continuously and quite spent to the overflow *l*. The steam travels in the opposite way—namely, along the steps of cone *i*, upwards in pipe *m*, and through *n* into the lime vessel *f*. From here the mixed steam and ammonia-vapours ascend into the column *e*, and traverse this from chamber to chamber, and ultimately leave it by the pipe *p*. This pipe enters the saturating box *d*, filled with sulphuric acid. The sulphuretted hydrogen, carbon dioxide, &c., collecting in the bell *g*, are led through the flue *s* into the economiser *b*, where they give up their heat to the gas-liquor, and lose their steam in the shape of condensed water. Ultimately they are conveyed by a pipe not shown in the diagram into some fireplace to be burned, or can be treated in any other desired way.

In the apparatus of Feldmann (G. P. 21,708) fig. 4, the gas-liquor, after having passed through the ordinary rectifying column *A*, flows into a vessel *B*, into which milk of lime is pumped by *C* in regular intervals, whilst the whole is kept agitated by steam injected into the mixture. The liquor, after having deposited most of the

lime, flows into a second column *C*, where the ammonia set free by the lime is distilled off: the spent liquor runs away continuously through *g*, and the gases and vapours pass over by pipe *e* into the first column *BA*, which serves both for

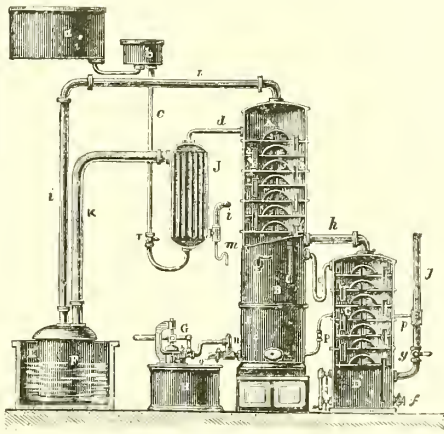


FIG. 4.

retaining the water and for driving off the volatile ammonium salts contained in the crude gas-liquor. The economiser *J*, and the saturator *J*, with the gas-bell *F*, require no special explanation. This apparatus, as well as those of Mallet and Grüneberg, is very successfully employed at many works.

All the apparatus described here are of the 'continuous' kind, but in many ammonia works intermittent stills are yet in use, mostly in sets of two or even three, the fresh liquor being fed into the top still and finding its way into the bottom still when this has been emptied. Such apparatus, as well as many other descriptions of ammonia stills, are described and figured in Lunge's *Coal-Tar and Ammonia*, Chapter 14. There are found there also descriptions of apparatus specially adapted for extracting the ammonia from the fermented sewage liquors and from the mother liquors of ammonia-soda works.

The gases obtained in all these apparatus consist of free ammonia, ammonium sulphide, and ammonium carbonate (or rather of a mixture of dissociated gases producing these compounds on condensation). Sometimes they are condensed at once in the shape of a concentrated solution, principally for the use of the ammonia-soda manufacturers, and sold as *concentrated gas-liquor*. More frequently they are utilised for the production of ammonium sulphate or ammonium chloride.

Ammonium sulphate is produced by passing the vapours evolved in the ammonia stills into 'saturators' containing sulphuric acid. These are generally wooden vessels, lined with lead; the vapours are admitted by a perforated pipe near the bottom, or by a bell-jar dipping below the liquid, or a similar contrivance. In any case care must be taken not to allow the offensive gases evolved during the evaporation, especially hydrogen sulphide, to escape into the atmosphere. It was formerly most usual to burn the hydrogen sulphide by passing it through



a coke fire, the sulphur dioxide being conducted into a chimney. But as the combination of ammonia with sulphuric acid evolves considerable heat, a great deal of steam is formed, which accompanies the hydrogen sulphide, and would interfere with its combustion unless it were previously removed. This is generally done by cooling the vapours escaping from the saturation, so that the steam is condensed, most rationally, by employing their heat for a previous heating-up of fresh gas-liquor. Several of the new stills (Grüneberg's, Feldmann's, &c.) have adopted this principle. A rather complicated apparatus for burning hydrogen sulphide is described by Chateau (Bl. 36, 195).

Usually, the sulphur dioxide formed by the combustion of hydrogen sulphide is allowed to escape into the air as being comparatively harmless. But this is only a makeshift, and should not be resorted to in large works, since it has been proved that the hydrogen sulphide can be burned so as to utilise the sulphur dioxide formed for the manufacture of sulphuric acid (P. Spence at Manchester, Hunt at Frizinghall near Bradford). Sometimes this hydrogen sulphide is burned in ordinary pyrites-burners together with pyrites or spent oxides (Spence, E. P. 1882, 1,494).

Young (E. P. 1880, 1,310) burns the ammonium sulphide directly into sulphate, and converts this into sulphate by means of heated air.

Attempts have been made to retain the hydrogen sulphide by lime, or to precipitate it with iron or manganese salts, but the former process is incomplete and the latter too troublesome and costly. It has also been proposed to employ ferrie hydrate in the still itself; the reaction would then be:

$$\text{Fe}_2(\text{OH})_6 + 3(\text{NH})_2\text{S} = 2\text{FeS} + \text{S} + 6\text{NH}_3 + 6\text{H}_2\text{O}.$$

The ferrous sulphide remaining behind is revived in the usual manner until it is saturated with free sulphur, which is then recovered by well-known processes.

The simplest and, in most cases, also a perfectly efficient plan is that of passing the saturator gases, previously freed as much as possible from moisture, through an ordinary oxide of iron purifier, such as is used at all gasworks. This completely retains the hydrogen sulphide.

It is preferable not to connect the purifier with a chimney, but to leave it open so that any imperfection in its action can be discovered at once before the noxious gases have travelled any distance. Of course the spent oxide is revived in the usual manner, and is ultimately worked for the sulphur it contains.

In the process of C. F. Claus (E. P. 3,606, 1882; 5,070 and 5,959, 1883) the gas is mixed with a carefully regulated quantity of air, containing just sufficient oxygen to burn the hydrogen of the hydrogen sulphide, and the mixture is passed through a chamber in which it has to traverse a hot layer of porous material, preferably oxide of iron. Here the hydrogen is burnt to water and sulphur is set free, the heat of the reaction keeping up the temperature without any external heating. The steam and sulphur vapours pass into a series of condensing chambers from which the sulphur is from time to time removed. Since at times some sulphur

dioxide or hydrogen sulphide, or both, may escape, the gases should be ultimately passed through limestone moistened with water and through a small oxide of iron purifier. This process is stated to work very satisfactorily.

Apart from the nuisance caused by the gases escaping from the saturators, there may be nuisance arising from the storage of the gas-liquor, from the evaporation of sulphate liquors, and more especially by the waste liquor from the stills, which contains much lime, together with tarry matters.

There are two systems of absorbing the ammoniacal vapours in sulphuric acid. When somewhat concentrated acid is used (say of sp.gr. 1.7) the ammonium sulphate separates out in the solid state, and can be fished out from time to time. The acid is run in continuously in a thin jet; all the excess of water is driven off by the heat generated by the reaction, so that no artificial evaporation is necessary. But as the liquor in this case has no possibility of settling out any impurities, the salt sometimes does not come out very pure. It is therefore frequently preferred to employ dilute sulphuric acid down to sp.gr. 1.4; the solution formed is clarified by standing, and is then evaporated to crystallisation, mostly in lead pans, by means of a steam coil. The mother liquor is employed for diluting a fresh quantity of sulphuric acid.

In England it was formerly most usual to employ sulphuric acid made from brimstone for this purpose, because the acid made from pyrites contains iron and arsenic, which discolour the ammonium sulphate. But as this is not material when it is to be employed as a manure, nearly all continental manufacturers, and latterly also many English makers, employ pyrites acid, only avoiding that made from Spanish pyrites, in which the amount of arsenic is excessive.

It is quite possible to get white ammonium sulphate from pyrites-acid by means of the following plan. To the acid employed at sp.gr. 1.71 a certain quantity of 'vitriol-tar' is added—that is, the sulphuric acid which has served for purifying crude benzol, and which is charged with a large quantity of pyridine bases and of tarry impurities. On the acid being saturated by the ammonia coming over, the tarry matters and the bases are separated and rise to the surface, carrying along and enveloping the arsenious sulphide formed at the same time from the pyrites acid. The scum is carefully removed, and the sulphate fished out after this is perfectly white. The tarry scum can be employed for recovering the pyridine series of bases, which have now been turned to several useful purposes.

A serious impurity sometimes found in commercial ammonium sulphate (even up to 91 p.c.) is ammonium thiocyanate, which is very injurious to vegetation. This is unlikely to be found in the salt obtained by the processes just described, but it may occur in the salt obtained by direct saturation of gas-liquor with acid, or in that made from the washings of the spent oxide of gas-purifiers. Such solutions ought not to be evaporated directly, but distilled with lime; the calcium thiocyanate formed can be extracted from the residue and utilised for commercial purposes.

Commercial sulphate of ammonia is sold according to its percentage of ammonia. Chemically pure salt would contain 25.75 p.c.; the commercial salt sometimes contains rather more than 25 p.c., and it ought not to fall below 23 p.c. This, of course, ought not to include ammonium thiocyanate, which can be easily detected by the red colouration imparted to its solution by a per-salt of iron. Ammonium sulphate is found in trade sometimes of nearly white colour, sometimes grey or even brown (from tarry matters), or greenish-yellow (from arsenic). The latter colour is objected to by most buyers. It is not usual to purify ammonium sulphate by recrystallisation, which of course could be very easily done if it were required.

**Ammonium chloride** (*muriate of ammonia*, *sal-ammoniac*) is obtained by saturating the gases evolved from an ammonia still with hydrochloric acid; but it is not quite so easy to do this in the same way as previously described with sulphuric acid, since lead vessels do not resist the action of hot hydrochloric acid, and stone or stoneware vessels are, for various reasons, awkward to employ. This is avoided by allowing the ammoniacal liquid to condense by itself, and then to meet a thin stream of hydrochloric acid, just sufficient to saturate the ammonia, the permanent gases being carried away as usual. The solution is boiled down to the crystallising point, either in leaden or iron vessels; in the latter case the liquor must always contain a slight excess of ammonia, since it would otherwise act upon the iron. Sometimes ammonium chloride is obtained by double decomposition of ammonium sulphate and sodium chloride; when mixing a concentrated solution of the former salt with an equivalent quantity of common salt, and boiling down, monohydrated sodium sulphate separates out, and ammonium chloride remains in solution.

The crude ammonium chloride is coloured by tarry matters, and always contains other impurities. In order to purify it, it is dried on metal plates heated by the waste heat of the subliming pans till the moisture and free acid are volatilised and the tarry matters are mostly carbonised. The roasted salt is quickly conveyed into the *subliming pans*, cast-iron pots of from 3 to 9 feet diameter, lined with fire-brick, and covered with thick concave metal plates. The covers are perforated in the centre so that the permanent gases may escape. These pans are heated till sublimation sets in, when the fire is slackened and carefully regulated—the temperature being kept neither too low nor too high—since in either case the sublimate is not of the proper colour, translucency, or fibrous texture. The operation lasts from 5 to 9 days; the cover is then raised, and a layer of sublimed sal-ammoniac is found on its lower side, from 2½ to 4 inches thick. That part of it which is immediately adhering to the iron is always brown, and is removed previously to sending out the salt.<sup>1</sup> The *sal-ammoniac* of commerce is sublimed ammonium chloride, whilst *muriate of ammonia* is the commercial term for ammonium

chloride, more or less purified by crystallisation in the wet way.

Sometimes it is recommended to mix the crude ammonium chloride, previously to subliming it, with animal charcoal or with phosphates, in order to purify it from tarry substances and from iron, but this does not appear to be done in practical work. If a product entirely free from iron is desired, the ferrous chloride contained in the crude salt should be converted into perchloride by passing chlorine through the boiling solution of the salt and precipitating the iron by ammonia. An excess of chlorine would produce nitrogen chloride, which must be carefully avoided on account of its explosiveness.

*Crystallised ammonium chloride*, commonly called *muriate of ammonia*, is much cheaper than the sublimed salt, and equally efficient for most purposes. It is made by dissolving the crude salt and filtering the solution through animal charcoal before allowing it to crystallise.

**Commercial ammonium carbonate** (*sal volatile*) is really a mixture or compound of ammonium bicarbonate and carbamate. It is usually made by mixing 1 part of ammonium sulphate with 1½ or 2 parts of calcium carbonate (ground chalk) and heating in horizontal cast-iron cylinders, first slowly, afterwards to redness. The vapours are conveyed into lead chambers, where they are condensed by air-cooling or by means of a water jacket. When a sufficiently thick crust has been formed by repeating the operation several times, it is loosened by blows from the outside and is removed by means of a door. A pipe at the bottom serves for running off a little solution of ammonium carbonate formed by the excess of moisture, and for the escape of steam. The product of this operation is still very impure, and is especially contaminated by tarry matters; it is therefore converted into a white salt by resubliming in iron pots surmounted by a leaden cap, in which the sublimed salts form white fibrous crusts.

The usual process for making ammonium carbonate does not appear quite rational, since according to the conditions of the process there is only enough CO<sub>2</sub> (3 molecules CO<sub>2</sub> to 4 molecules NH<sub>3</sub>) to form a neutral salt, whilst commercial ammonium carbonate corresponds to 1½ times as much CO<sub>2</sub>. Hanekop (Ar. Ph. 1886, 24, 21) has found some English commercial carbonate of ammonia to consist entirely of bicarbonate. This is, however, evidently an exception to the rule. Hence a large quantity of ammonia must go away in the uncombined state unless carbon dioxide in excess is passed into the condensing chambers. At Kunheim's works (near Berlin) the gaseous mixture from the distillation of gas-liquor is directly brought together with CO<sub>2</sub> in lead chambers, and thus the commercial salt is produced. Seidler (G. P. 26,633) distils gas-liquor directly with calcium carbonate. Teed (S. C. I. 1885, 709) has shown that a solution of ammonium chloride is completely decomposed by slowly trickling down a tower filled with pieces of calcium carbonate, steam being blown in at the same time, at the top of the tower solid ammonium carbonate was deposited.

<sup>1</sup> In France *sal-ammoniac* is made in earthenware or glass vessels, and is therefore purer than the English article made in iron pots, but it is more costly, the subliming vessels being destroyed at each operation.

**Caustic ammonia** (*liquor ammonia*) is made in the purest form by redistilling ammonium sulphate with lime. It is, however, much cheaper to make it directly from the gas-liquor stills, but in this case a large quantity of lime must be employed, and this must be added from the beginning in order to retain carbon dioxide and hydrogen sulphide. This is not quite easy, as calcium sulphide partially decomposes during the distillation; but this can be avoided or remedied by the use of ferric hydroxide, either in the ammonia stills or subsequently in special purifiers (compare above).

Kunheim (G. P. 26,422) treats the gas-liquor in the cold by a current of air, divided in many fine jets. This splits up the ammonium sulphide into free ammonia and hydrogen sulphide. The gases are passed through ferric hydroxide suspended in a solution of alkaline earths, where hydrogen sulphide is absorbed, whilst ammonia passes on. The FeS first produced is at once decomposed by the air into  $\text{Fe}(\text{OH})_3$  and free S.

When making caustic ammonia directly from gas-liquor, the apparatus of Grüneberg, of Feldmann, of Coffey, &c., cannot very well be employed, since the quantity of lime required to retain the carbon dioxide and hydrogen sulphide is too considerable. Hence, for this purpose, ordinary double stills are employed, the first of which is provided with strong agitating gear, and is charged with a great excess of lime; it receives the liquor previously treated in the second still. The latter is mounted on a higher level, and receives fresh gas-liquor previously heated up by some waste heat. The vapours issuing from the first still are passed through the contents of the second, which they raise nearly to the boiling-point, the liquid retaining a great deal of the steam. The vapours which escape absorption ought, before being condensed, to be further purified by passing through milk of lime and by a previous cooling, so that most of the steam is deposited as liquid water. It is only when nearly dry that they are fit for treating with wood-charcoal, which is done by passing them through a series of vessels charged therewith; this charcoal must, of course, be from time to time re-ignited. The purified gas is lastly condensed by means of water, internal and external cooling being employed at the same time.

Caustic ammonia made from gas-liquor directly, and, to a certain extent, even that made from ammonium sulphate, obstinately retains some tarry (empyreumatic) substances and compound organic volatile bases. The empyreuma can be removed by further treatment with ignited charcoal, or by distilling over potassium permanganate. The presence of such impurities is generally indicated by the smell of the liquor, and more distinctly by pouring a few drops of it into a test-tube containing colourless nitric acid diluted with a quarter of its volume of water, when a pink colour will appear; but the ammonia ought not to be added in such quantity as to saturate the free acids (Lehmann, W. J. 1864, 195; Kupferschläger, Bl. 23, 256; Wittstein, D. P. J. 213, 512). Caustic ammonia made from the liquor produced by fermenting urine is completely free from all those tarry impurities.

**Ammonium phosphate.** Monammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ), and diammonium phosphate ( $\text{NH}_4)_2\text{H}_2\text{PO}_4$ ) have become commercial products by the process of Lagrange, which starts from commercial superphosphate. This is lixiviated by water and steam, and a solution of sp.gr. 42°Tw. is obtained, together with a worthless residue of calcium sulphate. Some of the latter remains in the solution, and is removed by carefully adding barium carbonate. The filtrate is neutralised by ammonia in slight excess, whereby all the lime is precipitated as basic phosphate, which is washed and used over again for the manufacture of superphosphate. The filtered solution, marking 32°Tw., contains monammonium phosphate, and can be worked for this, or for diammonium phosphate. The latter is obtained by gradually mixing the above solution with *liquor ammonia* of sp.gr. 0·92, in the proportion of  $1\frac{1}{2}$  equivalents of  $\text{NH}_3$  to 1 of ( $\text{NH}_4\text{H}_2\text{PO}_4$ ). The diammonium phosphate at once separates out as a crystalline mass, which, after cooling, is submitted to hydraulic pressure. The operation is carried out in a closed vessel, to prevent the escape of ammonia. The mother liquor is employed for the manufacture of ammonia. The diammonium phosphate is principally used in Lagrange's sugar-refining process.

#### TECHNICAL APPLICATION OF AMMONIA AND AMMONIACAL SALTS.

**Caustic ammonia** is employed in pharmacy dyeing, calico-printing, for the preparation of colouring-matters and of many chemicals; especially also for Carré's and Linde's ice-making machines. The largest quantities of ammonia are used in the manufacture of soda by the ammonia process; but in this case the manufacturers start either from ammonium sulphate or from the strong crude liquid obtained in distilling gas-liquor (compare above).

**Ammonium sulphate** is mostly employed as a manure as a substitute for sodium nitrate. Although the nitrogen of the nitrate is generally cheaper than that of ammonium sulphate, the latter salt cannot be replaced by it in all cases, and is hence extensively employed, especially for the cultivation of sugar-beet. Large quantities are also used for the manufacture of alum, for the ammonia-soda process, and for preparing caustic ammonia and the other ammonium salts.

**Ammonium chloride** (*sal-ammoniac*) is used in pharmacy, in soldering, in galvanising iron, in dyeing and calico-printing, and for a variety of less important purposes. Its uses are very much more restricted than those of the sulphate.

**Ammonium carbonate** is used for scouring wool, in dyeing, as a baking powder, &c.

**Statistics.**—Great Britain produces most of the ammoniacal compounds found in trade. Mr. Fletcher's twenty-third Report on the Alkali &c. Acts (26) states the amount of sulphate, together with a small quantity of muriate of ammonia, produced in 1886 in the United Kingdom as under:—

Gas-works . . . . .	82,480
Iron-works . . . . .	3,950
Shale-works . . . . .	18,030
Coke and carbonising works . . . . .	2,100
Total . . . . .	106,510



Besides about 1,000 tons of sal-ammoniac, only about 22,000 tons of that quantity is retained for home use, the remainder being exported, the largest customer being Germany. That country herself produces about 10,000 tons, France 12,500 tons, Holland and Belgium 3,000 tons, the United States of America 11,000 tons of sulphate of ammonia. All these countries import, almost entirely for agricultural purposes, much more from England than they produce themselves.

G. L.

**AMMONIACUM, AFRICAN**, *v.* GUM RESINS.

**AMMONIACUM, GUM**, *v.* GUM RESINS.

**AMMONIACUM, PERSIAN**, *v.* GUM RESINS.

**AMMONIUM MELEQUETA** *v.* COCCULUS INDICUS.

**AMRAD-GUM.** The gum forms white, yellow, and brown lumps of a sweetish taste and resinous smell. An aqueous solution (1 : 2) is viscid and strongly adhesive. It also gives with oil excellent emulsions, which keep very well. The dry substance contains 5.61 p.c. of ash, consisting of carbonic acid, lime, iron, magnesia, traces of phosphoric acid and silica. Has been recommended as a substitute for gum arabic. It was brought into the market some years ago, and comes from the Abyssinian highlands; is probably obtained from *Acacia Abieca* (Schweinfurth). (H. Unger and Kempf. Pharm. Zeit. 33, 218; S. C. F. vii. 446.)

**AMYGDALIN** *v.* GLUCOSIDES.

**AMYL ALCOHOL**  $C_5H_{12}O$ . The ordinary amyl alcohol (fusel oil, fermentation amyl alcohol, or isoamyl alcohol) is one of the eight alcohols of the formula  $C_5H_{12}O$  theoretically possible, and is the chief constituent of the fusel oil or 'last runnings' obtained in the rectification of alcohol, particularly of the alcohol made by the fermentation of potatoes. Amyl alcohol is apparently an invariable constituent of the product obtained when ordinary alcohol is fermented by fermentation; but the precise conditions attending its formation are not known. The alcohol is got from the 'last runnings' by shaking the crude product with hot milk of lime, decanting, drying over calcium chloride, and rectifying at a temperature of  $132^\circ$ .

*Properties.*—Amyl alcohol is a colourless liquid with a peculiar cough-exciting odour and a burning taste; it burns with a white smoky flame. Its b.p. =  $131.6^\circ$  (cor.) and sp.gr. = 0.8248 at  $0^\circ$ , = 0.8113 at  $18.7^\circ$  (Kopp, A. 94, 289); b.p. =  $128.9^\circ$ – $129.2^\circ$  at 740.9 mm., and sp.gr. = 0.8104 at  $20^\circ$  (Brühl, A. 203, 23); b.p. =  $130.5^\circ$ – $131^\circ$  at 759.2 mm. (Schiff, A. 220, 102). It is soluble in ethylic alcohol and ether, but is soluble in water only to the extent of 1 in 39 at  $16.5^\circ$  (Wittstein, J. 1862, 408), and 1 in 50 at  $13^\circ$ – $14^\circ$ , and the solution becomes milky at  $50^\circ$  (Balbiano, B. 9, 1437). Amyl alcohol dissolves in all proportions in acetic acid diluted with an equal bulk of water (Berthelot and St. Gilles, J. 1862, 403). When oxidised with platinum black ordinary valeric (isovaleric) acid is formed, whilst distillation with either manganese dioxide or potassium dichromate and sulphuric acid converts it into isovaleraldehyde and isovaleric acid. Sulphuric acid dissolves it in the cold forming amylsulphuric acid, which, on heating, decomposes into amylene and its polymers diamylene and

tetramylene; these hydrocarbons, together with hexylene and the corresponding paraffins, are also obtained when amyl alcohol is distilled with zinc chloride (Bauer, Z. C. P. 1861, 645; Wurtz, A. 123, 316); it is probable, however, that the latter owe their formation to impurities in the alcohol. The action of chlorine has been studied by Barth (A. 119, 216), and that of bleaching powder by Goldberg (J. pr. [2] 24, 116). The bromide (Cahours, A. 30, 298; Balbiano, J. 1876, 348), chloride (Cahours, A. 37, 164; Balard, A. 52, 312; Balbiano, *l.c.*), and iodide (Cahours, A. 30, 297) have been prepared by the action of the corresponding phosphorus compounds. Commercial amyl alcohol is generally levorotatory; the degree of rotation, however, is not constant, but varies in different specimens, and the variation has been shown by Pasteur (A. 96, 255) to be due to the fact that ordinary amyl alcohol is a mixture, in varying proportions, of two isomerides, one of which is optically inactive, and the other levorotatory. When ordinary amyl alcohol is treated with sulphuric acid and the resulting amyl-sulphuric acids converted into barium salts by neutralisation with barium carbonate, a separation of the two isomeric alcohols can be effected, inasmuch as the barium salt of the optically active alcohol is  $2\frac{1}{2}$  times more soluble in water than the corresponding salt of the optically inactive modification. This question has been further examined by Ley (B. 6, 1362), Le Bel (B. 9, 358), Bakhoven (J. pr. [2] 8, 272), Chapman (Z. 1870, 406), and Pedler (C. S. 21, 74), with results which do not entirely agree; whilst Wyschnegradsky (A. 190, 366) is of opinion that a third isomeride, normal amyl alcohol, is also present.

In addition to the optically active and inactive modifications obtained from ordinary amyl alcohol, the following isomeric alcohols have been prepared:—*Normal amyl alcohol* (Lieben and Rossi, A. 159, 70; Schorlemmer, A. 161, 268); *methylpropyl carbinol* (Schorlemmer, *l.c.*; Saytzev and Wagner, A. 175, 351; 179, 313; Markownikow, J. 1883, 861); *methylisopropyl carbinol* (Wyschnegradsky, *l.c.*; Münch, A. 180, 339; Winogradow, A. 191, 125); *diethyl carbinol* (Saytzev and Wagner, *l.c.*); *dimethylethyl carbinol* (Wurtz, A. 125, 114; 127, 236; 129, 365; Berthelot, A. 127, 69; Flavitzky, A. 179, 348; Wyschnegradsky, *l.c.*; Osipoff, B. 8, 1240).

**$\alpha$ -AMYLAN**  $nC_5H_{10}O_5$  (O'Sullivan, C. J. 41, 24). A carbohydrate found in the cereals wheat, rye, barley, and oats, but most plentifully in the two latter. It is a gum-like body, only slightly soluble in water, a 2 p.c. solution forming a jelly-like fluid; a 1 p.c. solution flows freely, however, and is transparent. It is insoluble in alcohol. The solution in water is optically active, the apparent sp. rotation being  $[\alpha]_D = -24^\circ \pm 2^\circ$ . Digestion with sulphuric acid converts it directly into dextrose. It is probably owing to the presence of this body that unmaltd barley cannot be satisfactorily employed in the preparation of beer. Malted grain does not contain it. Distillers using raw grain (oats and barley) have at times much difficulty in separating the wort (solution of sugars, &c.) from the grains (undissolved portion of the grain employed) in consequence of the presence of this body in

quantity, the barleys and oats of some seasons containing much more of it than at other times.

**β-AMYLAN**  $nC_5H_{10}O_5$  (*l.e.*). A carbohydrate from the same source as the  $\alpha$ -compound. It exists in larger quantity in wheat and rye than in barley and oats, and a substance agreeing very closely with it in general properties is found in malted barley. It is more soluble in water than  $\alpha$ -amylan, insoluble in alcohol, but, when pure, forms with that liquid a *milk* without being precipitated. A drop of acid coagulates the milk, throwing the amylan out of solution. Digestion with sulphuric acid converts it directly and quantitatively into dextrose. Its optical activity is  $[\alpha]_D = -72^\circ$ ; but digestion with lime-water raises the activity to  $[\alpha]_D = -144^\circ$ .

If this and the  $\alpha$ -compound could be economically prepared from distillers' wash, a use would probably be found for them in dressing crape, lace, &c. C. O'S.

**AMYLENE**  $C_5H_{10}$ . Five isomeric amylenes are theoretically possible, and all have been prepared. These hydrocarbons have been chiefly studied by Flavitzky (A. 179, 340) and by Wychnegradsky (A. 190, 336), and can be obtained by the action of alcoholic potash on the various amyl iodides, or by the action of dehydrating agents such as sulphuric acid or zinc chloride on amyl alcohol.

The amylene ordinarily met with is trimethylethylene, and is chiefly obtained by the dehydrating action of zinc chloride on fermentation amyl alcohol.

**Preparation.**—To prepare amylene, fermentation amyl alcohol (1 part) is shaken with coarsely-powdered zinc chloride ( $1\frac{1}{2}$  parts), allowed to remain for twenty-four hours, and then distilled. The product consists of a complex mixture of paraffins from  $C_4H_{10}$  to  $C_{10}H_{22}$  with olefins from  $C_4H_8$  to  $C_{10}H_{20}$  (Wurtz, J. 1863, 507). These can be isolated by fractional distillation (Wurtz), but according to Eltekow (J. R. 14, 379) amylene is most readily obtained if the product is well cooled, and shaken with dilute sulphuric acid (2 vols. of acid to 1 vol. of water), the acid layer separated, diluted with water, and distilled; the distillate consists of amylene (trimethylethylene) and tertiary amyl alcohol, and the latter, on distillation with sulphuric acid (1 : 1) yields pure trimethylethylene.

Other methods for obtaining ordinary amylene have been described by Balard (A. Ch. [3] 12, 320), Bauer (J. 1861, 659), and Linnemann (A. 143, 350).

**Properties.**—Amylene is a colourless liquid b.p.  $36^\circ-33^\circ$  and sp.gr. 0.6783 at  $0^\circ$  (Le Bel, Bl. 25, 517); b.p.  $36.8^\circ$  at 752.7 mm. (Schiff, A. 223, 65). It combines directly with a large number of substances: with nitric peroxide (Guthrie, C. S. 13, 129; Wallach, A. 241, 201; 243, 161; Miller, Proc. C. S. 3, 108), sulphur chloride and chlorine (Guthrie, C. S. 12, 112; 13, 45, 129; 14, 136), with bromine (Wurtz, A. Ch. [3] 55, 458), and, when cautiously mixed with well-cooled sulphuric acid, sp.gr. 1.67 (2 vols.  $H_2SO_4$  to 1 vol. water), in a freezing mixture, is converted into dimethylethyl carbinol, which can be obtained, after neutralisation with sodium hydroxide, on distillation (Flavitzky, 175, 157); with sulphuric acid sp.gr. 1.545 (2 pts. by weight  $H_2SO_4$  to 1 pt. water)

methylethyl carbinol is obtained (Osipoff, B. 8, 542, 1240).

In addition to ordinary amylene, the following isomerides have been obtained:—*Normal amylene*, b.p.  $39^\circ-40^\circ$  (Wurtz, A. 123, 205; 127, 55; 148, 131; Flavitzky and Wychnegradsky, *l.e.*); *isopropylethylene*, b.p.  $= 21.1^\circ-21.3^\circ$  (Flavitzky and Wychnegradsky, *l.e.*); *symmetrical methylethylethylene*, b.p.  $= 36^\circ$  at 740.8 mm. (Wagner and Saytzev, A. 175, 373; 179, 302); and *unsymmetrical methylethylethylene*, b.p.  $= 31^\circ-32^\circ$ , sp.gr.  $\approx 0.67$  at  $0^\circ$  (Wychnegradsky, *l.e.*; Le Bel, Bl. 25, 546).

The action of hydrogen iodide on the amylenes has been investigated by Saytzev (A. 179, 126); whilst Zeidler (A. 186, 245) has examined the products obtained when various amylenes are oxidised with potassium permanganate in acid, neutral and alkaline solution, with chromic acid, and with potassium dichromate and sulphuric acid.

The following polymerides of amylene have also been obtained, and can be prepared by heating ordinary amyl alcohol or amylene with zinc chloride:—*Diamylene*  $C_{10}H_{20}$  (Balard, A. 52, 316; Schneider, A. 157, 207; Bauer, J. 1861, 660); *triamylene*  $C_{15}H_{30}$  (Bauer, *l.e.*); and *tetramylene*  $C_{20}H_{40}$  (Bauer, *l.e.*).

#### AMYRIN v. OLEO-RESINS.

**ANACAHUITA.** A wood of unknown botanical origin imported from Mexico; its preparations are said to be useful in pulmonary disorders. The wood contains a volatile oil, an iron-greening tannin, gallic acid, a yellowish resin, sugar, a tasteless volatile body crystallising in warty masses, and a bitter substance crystallising in white needles (J. 1861, 771).

**ANACARDIUM NUT.** *Cashew nut, Kajoo.* A nut which is edible after it has been roasted to expel the cardol it contains; the cardol thus obtained is used at Goa for tarring boats (Dymock, Ph. [3] 7, 730). In addition to cardol the nuts contain *anacardic acid*, and an oily matter which, by exposure to the air, assumes a fine black colour, permanent against acids, alkalis, chlorine, and hydrocyanic acid. It has been recommended as a marking ink, and is used for giving a black colour to candles (Böttger, D. P. J. 205, 490).

**ANALYSIS.** Analysis is the separation of a complex substance into its constituents. It is *proximate* when a mixture is separated into the compounds of which it is composed, *ultimate* when those compounds are separated into their constituent elements. It is *qualitative* when the nature only of the constituents is ascertained, *quantitative* when their amount is determined.

For the purposes of research the most accurate methods are naturally selected and other considerations are of secondary importance, but for technical purposes extreme accuracy is rarely required, and in many cases a method which will give an approximately correct result in a short time is of greater value than a more accurate method which requires a long time for its execution. This article is written mainly from a technical point of view, and an endeavour has been made to select the simplest and most rapid methods capable of yielding good results. For the same reason details of the separation of the rarer elements are omitted from the general

scheme for qualitative analysis. A list of special tests is, however, given, and from these the required method of separation can be framed.

### General operations.

Accuracy and rapidity in analysis are largely dependent upon attention to those general processes and methods of manipulation which are involved in almost every analytical operation.

*Sampling.*—It is of the highest importance that the sample under examination should be truly representative of the bulk of the substance. Discrepancies between the results of different analysts are usually attributed to inaccurate methods or inaccurate work, but in many cases they are really due to imperfect sampling. If the substance is a liquid, the contents of the vessel should be thoroughly mixed before the sample is withdrawn. If the substance is contained in several vessels, a proportional quantity should be taken from each, the different portions mixed together, and the final sample taken from the mixture.

In the case of solid products care must be taken to secure a proper proportion of large and small, hard and soft fragments. If a ship's cargo is to be sampled, portions should be taken from different parts of the bulk; if the substance is contained in railway trucks, portions should be taken from the ends and middle of each truck. When the substance is in bags or barrels a long hollow auger is thrust to the bottom of each and then withdrawn, bringing with it a long core of the substance. If the material loses or gains moisture, or undergoes any other change on exposure to air, as in the case of soap or caustic soda, a proper proportion of the internal and external portions must be taken. In all cases the first samples are broken into small pieces, thoroughly mixed, and one-fourth taken for further treatment. This is ground to powder, again thoroughly mixed, and one-fourth taken. The subdivision is repeated if necessary, and the final sample kept in well-closed bottles.

If the mixture is soft and friable, pulverisation is readily effected in a porcelain or earthenware mortar, but harder substances should be powdered in a cast iron or steel mortar. When

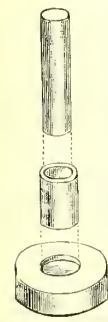


FIG. 1.

the piston is placed inside and struck smartly with a hammer, which drives it down upon the mineral. The final crushing is done in an agate mortar.

*Drying.*—Many substances absorb more or less moisture when exposed to the air, and in order to bring them into a definite condition for analysis, it is desirable that they should be dried, this operation being conducted at the ordinary or at a higher temperature according to circumstances. Substances which contain water in combination are usually dried by exposure to air or by pressure between folds of filter paper. In other cases where a higher temperature would be injurious the substance may be placed under a bell-jar which also incloses a dish containing sulphuric acid. The operation proceeds more quickly if the bell-jar is connected with an air-pump and thus rendered vacuum.

Substances which do not decompose at 100° are best dried in a copper oven provided with a jacket containing water which is heated to boiling, the water-level being kept constant by means of an overflow and feeding arrangement at the side. The inside of the oven is fitted with a perforated shelf which supports dishes, funnels &c.

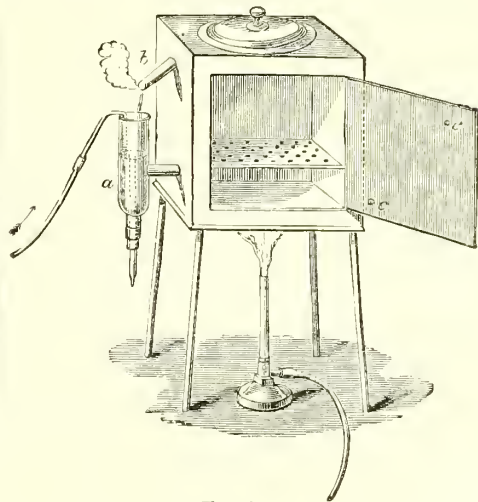


FIG. 2.

When the substance is sufficiently stable it is advisable to dry at 115–120°, since an increase of 10° or 20° often greatly reduces the time required. For this purpose we use a copper oven without a jacket, heated by a lamp underneath. Inside the oven at a little distance from the bottom is a shelf which supports the vessel containing the substance. At the top of the oven are two apertures, one of which serves to promote a current of air through the oven, whilst the other carries a thermometer the bulb of which is close beside the vessel which is being heated.

If it is desired to keep the temperature constant for a long time, the oven must be provided with a thermoregulator (*v.* THERMOREGULATORS).

*Weighing.* The balance and the precautions to be observed in weighing form the subject of a special article (*v.* BALANCE). As a rule substances taken for analysis should be weighed from tubes provided with well-fitting stoppers or corks, the difference between the weight of the



tube before and after the removal of the substance giving the weight taken for analysis. The quantity required for an analysis will depend upon circumstances. When constituents present in minute quantity have to be estimated, a relatively large amount of the substance is required, but for the estimation of one or two constituents from 1 to 2 grams of the substance is usually sufficient. The smaller the quantity of matter operated upon, the shorter the time required for filtration, washing, &c., but also the greater the demands on the skill and accuracy of the operator.

**Hygroscopic substances and precipitates** must be kept under a *desiccator*, i.e. a glass dish containing sulphuric acid or calcium chloride, fitted with a tray to support a crucible &c., and provided with an air-tight glass cover, preferably bell-shaped. Crucibles containing non-hygroscopic precipitates may be allowed to cool with exposure to air, provided that the empty crucible was allowed to cool under the same conditions before weighing.

**Solution.**—The solution of a substance is most conveniently effected in flasks or in somewhat deep beakers which are inclined at an angle in order to prevent possible loss by spurt-ing. The operation may be accelerated by heat, and the reagent should be used in the most concentrated form possible and in the least possible excess, in order to avoid loss of time in evaporation &c. Evaporation to expel excess of solvent should, where possible, be conducted in the same vessel.

**Evaporation.**—The evaporation of a liquid may be effected over an ordinary flame, care being taken that the liquid does not boil. If

the lid of the crucible across the mouth of the vessel and thus producing a circulation. The rate of evaporation, *ceteris paribus*, depends on the area of surface exposed, and hence the operation is effected most quickly in shallow dishes, especially if a current of air removes the vapour as fast as it is given off. During the process the contents of the dish should be protected from dust &c., and this is readily done by supporting at a distance of about six inches above the surface of the dish a triangle of glass rod or tubing on which is stretched a sheet of filter paper freed from soluble compounds by treatment with acid. When evaporation over a direct flame is impracticable, the dishes &c. should be placed on a *water bath*, that is, a vessel containing boiling water, in such a way that they are heated by the steam. The top of the water drying-oven already described (fig. 2) may be provided with a series of rings of various sizes and thus serves two purposes. Ordinary tin cans or copper vessels of similar shape will answer, but in all cases it is desirable to have an arrangement for keeping the water at a constant level.

**Precipitation** is conducted in beakers, dishes, or conical flasks, but not in ordinary round flasks because of the difficulty of removing the precipitate. Glass vessels, especially when new, are appreciably attacked and dissolved by water, and still more strongly by alkaline solutions, the action increasing with the concentration of the solution and the duration of contact. Acid liquids, with the exception of dilute sulphuric acid, have less solvent action. Porcelain vessels, especially after they have been used for a short time, are not appreciably attacked. (Fresenius's Quant. Anal.; Emmerling, A. 150, 237). All precipitations involving long heating with alkaline liquids should be conducted in porcelain vessels or in platinum, silver, or nickel dishes.

Unless circumstances forbid, the liquid and the reagent should be heated to boiling and mixed gradually with continual agitation, since under these conditions precipitation as a rule is more rapid and complete, and the precipitate is obtained in a dense and granular form and is readily separated and washed. It is only in rare cases that prolonged standing after precipitation is necessary. Usually filtration may be commenced as soon as the supernatant liquid is clear, or at any rate after two or three hours. An unnecessary excess of reagent should always be avoided, but in all cases complete precipitation should be proved by adding a small quantity of the reagent to the clear liquid.

**Filtration.**—The separation of a precipitate from a liquid is usually effected by means of a specially prepared variety of blotting paper, known as filter paper. The Swedish paper made by J. Munktell has the oldest reputation, but that made by Schleicher and Schull, of Düren, is of excellent quality, and for many purposes answers better. The latter firm supply paper which has been treated with hydrochloric and hydrofluoric acids and thus freed from almost all inorganic matter. It is desirable that all paper used in quantitative work should be free from soluble compounds, and this end is secured by soaking the ordinary filter paper for

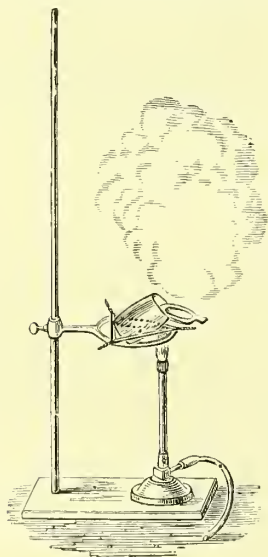


FIG. 3.

the operation is conducted in a flask or crucible, the latter should be inclined in order to prevent loss by ebullition, and the operation is accelerated in the first case by drawing a current of air through the flask, in the second by inclining

three or four hours in pure hydrochloric acid diluted with 15-20 times its volume of water, and then washing thoroughly to remove all traces of acid and soluble salts. The paper is conveniently kept in circular pieces of known radii (2, 4, 5, 6, 8, cm.) and the ash left by each size should be determined once for all by incinerating six filters of one of the medium sizes in the manner described under the treatment of precipitates, and weighing the ash which is left. This quantity divided by six gives the average amount of ash left by one filter of that size, and the amount left by the other sizes is readily calculated, the quantity of ash being proportional to the area of the paper.

Usually the filter paper is supported in a glass funnel which should have smooth even sides and an angle of  $60^\circ$ . The stem should be somewhat long and not too wide, with the lower end cut obliquely. A circular filter is folded in half, then in a quadrant, and when the quadrant is opened at one side it forms a hollow cone which should fit accurately into the funnel. The edge of the filter paper should be about 10 mm. below the edge of the funnel, and the size of the filter should be such that it is not more than three quarters filled by the precipitate. After placing the filter in position it is moistened with water, and fitted accurately to the glass, care being taken to remove all air bubbles from between the glass and the paper. Attention to these points greatly facilitates the subsequent filtration. The edge of the vessel containing the liquid to be filtered is slightly greased outside and the liquid is directed into the filter by means of a glass rod, care being taken not to disturb the precipitate until most of the clear liquid has passed through. It is advisable to keep the filter well filled with the liquid, but the latter must not rise higher than 10 mm. below the top of the paper.

In order to accelerate filtration a glass tube about 3-4 mm. in diameter and not less than 20 cm. long, bent into a loop near its upper end, may be attached to the stem of the funnel by means of indiarubber tube.

Greater rapidity of filtration is obtained by using one of the numerous water pumps (*v. FILTER PUMP*). In this case the liquid is filtered into a flask with stout walls, preferably of the conical form. The stem of the funnel passes through a cork which fits in the neck of the flask and also carries a tube connected with the pump, or the flask may be provided with a side tube for this latter purpose. When it is required to filter into a dish or beaker, the latter is placed under a tubulated bell jar standing on a glass plate, the cork carrying the funnel &c. being fitted into the tubulus of the bell jar. If the reduction of pressure is considerable, it becomes necessary to support the apex of the filter. In the case of filters of medium size the necessary toughness is obtained by dropping into the apex of the dry filter, after it has been fitted into the funnel, two or three drops of the strongest nitric acid. After a minute or two the paper is washed and is ready for use. Bunsen's original method is to support the apex of the filter by means of a cone of platinum foil, which is made in the following way. A circular piece of thin platinum foil 3-4 cm. in diameter is cut in the

manner shown in the diagram, softened by heating in a flame, and then placed against a small metal cone of  $60^\circ$  so that the point *a* coincides with the apex of the cone. The foil is then folded round the metal so that it also forms a small cone, which is finished by being pressed

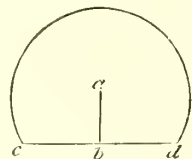


FIG. 4.

in a hollow conical mould into which the metal cone fits. It is then dropped into the funnel and the paper fitted in. The metal cones and moulds required can be purchased; Bunsen's method of making a cone and mould of plaster is described in Thorpe's Quantitative Analysis.

Carmichael has described a method of reverse filtration (*Z. N. F.* 6, 481; *Fr.* 10, 83). A stout bulb 25 mm. diameter is blown at the end of a glass tube about 2 mm. diameter, and the lower part of the bulb is flattened. Whilst still soft the flat part is pierced with a large number of small holes by means of a white-hot steel wire, care being taken that all the holes are at least 3 mm. from the edge of the disc. Platinum 'roses' of similar size, fused to short pieces of platinum tube about 2 mm. in diameter, can be purchased, and are more convenient and much less liable to fracture. The rose need not be hemispherical but may with advantage be much flatter in cross section. It is attached by means of a short piece of India-rubber tube to one limb of a glass tube which is bent twice at right angles, the other limb being fitted by means of a cork or air-tight cover to a flask or beaker which is also in communication with a pump (*C. J. Trans.* 1885, 123). A disc of filter paper is placed on the flat surface of the rose and moistened with water. The pump is then set in action, and the rose with its disc is introduced into the liquid to be filtered, care being taken that it does not touch the bottom. When the clear liquid has all been drawn off, the rose is raised, the pump being kept in action, fresh water is added to wash the precipitate and the rose is again introduced. After the precipitate has been washed and transferred to the vessel in which it is to be weighed, the paper disc with its adhering precipitate is readily detached from the rose. This method is very rapid; it is especially useful for precipitates which subside readily and when it is desired to keep a precipitate or residue in the original vessel. The filter paper is so small that the ash which it leaves on incineration is negligible.

Gooch (*C. N.* 37, 181) uses asbestos felt and a crucible with a perforated bottom. The asbestos makes an excellent filter, is not affected by ordinary acid and alkaline liquids, is readily dried, and does not alter in weight when ignited. Silky asbestos is scraped into a short fine down, boiled with hydrochloric acid, well washed and kept in water. A platinum crucible, preferably

of the low wide form, with the bottom perforated with a large number of minute holes, is fitted airtight into an ordinary funnel by means of an india-rubber ring placed between the crucible and the wall of the funnel, which is fitted into a filtering flask. The pump is set in action and water containing the asbestos in suspension is poured into the crucible. A layer of asbestos felt is quickly formed, and when this is of sufficient thickness it is drained, dried, and ignited over a lamp, and the crucible is then weighed. It is desirable to have a non-perforated bottom to fit on the crucible during ignition in order to protect the contents of the crucible from the flame gases. In cases where the use of platinum is inadmissible, a porcelain crucible perforated in a similar manner must be used. The weighed crucible is replaced in the funnel and filtration is conducted in the ordinary way, care being taken that the pump is set in action before any liquid is poured into the crucible. Drying and igniting the precipitate occupies but little time. For gelatinous precipitates the crucible may be replaced by a cone, the lower part of which is made of platinum gauze and the upper part of platinum foil.

Gooch has proposed (P. Am. A. 1885, 390; Fr. 24, 583) in special cases to replace the asbestos by anthracene, which after filtration can be dissolved in benzene or other suitable solvent, leaving the precipitate undissolved.

Not unfrequently it is necessary to keep the contents of a funnel hot during filtration. This is effected by placing the funnel inside a copper jacket filled with water which is heated to boiling by means of a side tube. A simpler plan is to coil lead pipe round the funnel and blow steam through the pipe (Richter, J. pr. N. F. 28, 309).

Sometimes it is desirable to avoid contact with air during filtration. A convenient apparatus for this purpose has been described by Klobukow (Fr. 24, 395; S. C. I. 4, 756).

All precipitates require to be washed in order to remove soluble impurities, the liquid employed being water, dilute acid, dilute ammonia, alcohol, &c., as the case may require. The object in all cases is to reduce the impurity to the desired minimum in the shortest possible time with the least expenditure of liquid, and it can readily be shown that successive treatments with small quantities of the liquid are far more effectual than the same volume of liquid applied all at once (Bunsen, A. 148, 269). Whenever possible hot liquids should be used. The soluble impurity collects round the top edge of the filter paper by reason of capillary action and evaporation, and hence, when washing is effected with the aid of an ordinary wash-bottle with a movable jet, it is important that the liquid should be directed on to the top edge of the filter. It is also important that each quantity of wash-water should be drained away as completely as possible before adding a fresh quantity, and it is obvious that this takes place most readily when a pump is used. In this case the liquid is poured into the funnel from an open vessel to a height of about 10 mm. above the edges of the paper. Care must be taken that the precipitate is not drained so far that channels are formed. It is always advisable to ascer-

tain whether the washing is complete by testing a few drops of the last wash-water.

*Drying and weighing precipitates.*—Occasionally a precipitate must be dried without the application of heat, and this is accomplished in a desiccator over sulphuric acid, preferably in a vacuum. In other instances the substance is not injured by a temperature of say 120°, but cannot be ignited. In these cases the filter is carefully dried at the particular temperature, inclosed between a pair of watch-glasses, and weighed. It is then placed in the funnel and the operation proceeded with. After filtration the filter and the precipitate are thoroughly dried at the same temperature as before and again weighed, the increase being the weight of the precipitate. The majority of the precipitates usually met with can, however, be dried by heating them in a crucible over a lamp. In most cases it is not necessary that the precipitates should previously be dried. The greater part of the water is removed by draining in the funnel by means of the pump or by placing the filter and its contents on a porous tile or on a pad of filter paper. The filter is then introduced into a crucible, heated cautiously until quite dry and then heated more strongly until the weight is constant.

When the precipitate is not easily reducible it is not necessary to remove the paper before ignition. If any slight reduction takes place, for example, with barium sulphate, it is easily remedied by adding a few drops of dilute sulphuric acid and again heating. In the case of magnesium pyrophosphate strong nitric acid serves a similar purpose. If, however, the precipitate is readily reduced in contact with organic matter, it must be removed from the paper as completely as possible by gentle friction, and transferred to the crucible, which should stand on a sheet of glazed paper. A carefully trimmed feather or a camel's-hair brush is useful to transfer scattered particles from the paper to the crucible. The filter paper is then folded with the portion to which the precipitate had adhered inside, wrapped in platinum wire which forms a sort of cage, and set on fire. Whilst burning it is held over the crucible, and *when completely burnt out*, the ash is heated with the tip of a Bunsen flame for a few minutes and then shaken into the crucible.

Precipitates which contain compounds of silver, lead, zinc, tin, and other easily reducible metals, should be heated in porcelain crucibles, since platinum vessels are liable to be attacked. Care should also be taken that platinum vessels are not heated with smoky or 'roaring' flames, and do not come in contact with brass crucible tongs or easily fusible metals whilst hot. After some time the surface of the metal may become dull owing to the partial disaggregation of the platinum, but this defect can be remedied by polishing the metal with sea-sand or a burnisher.

*Heating appliances.*—The ordinary Bunsen burner serves for most operations, but the argand Bunsens introduced by Fletcher are more efficient, and the radial slit burner of the same inventor is perhaps the most efficient gas-burner for heating purposes that has yet been made. Glass vessels are more safely heated on a sheet of wire gauze or on a layer of sand in a metal tray. A



most useful piece of apparatus in a technical laboratory is a large iron plate supported on iron legs, and heated by a burner underneath the middle. Vessels placed on the plate near its edges are subjected to a very gentle heat, but may be raised to a much higher temperature by being moved nearer to the middle.

A water-bath provided with a constant feeding arrangement is the most useful way of heating vessels at 100°. If higher temperatures are needed, a saturated solution of calcium chloride, melted paraffin, or oil may be used. Maumené (C. R. 97, 45, and 215) has proposed to use fused mixtures of alkaline nitrates for temperatures between 140° and 250°. Brauner (C. J. 47, 887) has described a simple arrangement for heating substances in sulphur vapour.

*Reagents.*—The ordinary acids and ammonia are required in a dilute as well as in a concentrated form; they may be conveniently diluted with three times their volume of water. Ordinary solid reagents are dissolved in water and diluted so that 10 parts of the solution by measure contain 1 part of the salt by weight; it is then easy to calculate approximately the quantity of reagent required to precipitate a given amount of a substance. Special reagents will be described in connection with the various processes.

#### Proximate analysis.

The methods to be adopted for the separation of the constituents of any particular mixture will depend entirely upon the nature of the mixture. It is only possible to describe the general methods which are found to be most useful.

*Fractional distillation* is available for the separation of liquids which differ considerably in their boiling points (*c.* DISTILLATION).

*Fractional precipitation* may be employed for the separation of substances, some of which are precipitated by a given reagent, whilst the others are not; or for the separation of substances which differ in the order of their precipitation. If, for example, silver nitrate is added in successive small quantities to a solution containing an iodide, bromide, and chloride, the first portion of the precipitate contains the greater part of the iodine; the middle portion contains the greater part of the bromine, and the last portion the greater part of the chlorine. In a similar manner organic acids can, not unfrequently, be separated by taking advantage of differences in the order of their precipitation by silver nitrate or lead acetate. In these cases the separated precipitates can be suspended in water and decomposed by hydrogen sulphide, when the acids are again liberated.

*Fractional crystallisation* may be adopted in the case of substances which differ in their solubility in one and the same solvent. The solution is concentrated somewhat, and the crystals which separate are removed; the mother liquor is still further concentrated, and the second crop of crystals is removed, this process being repeated as often as the case demands. The least soluble compound is mainly in the first crop of crystals; the most soluble is in the last mother-liquor.

*Fractional saturation* is an analogous process, but is of more limited application. It was employed by Liebig for the separation of volatile

organic acids. The mixture of acids is mixed with a quantity of soda or potash insufficient for complete saturation, and is then distilled. The acids of higher molecular weight are first neutralised and converted into salts, which of course remain in the retort, whilst the acids of lower molecular weight are found in the free state in the distillate. Anything like complete separation is only to be obtained by many repetitions of this process.

*Fractional solution.*—The most useful and most generally applicable method of proximate analysis is based upon the different solubilities of various substances in different menstrua. The mixture is treated successively with various solvents, each of which dissolves some of the constituents, but leaves the others undissolved. Advantage may also be taken of the fact that the solubilities are in many cases modified by a rise of temperature. Further, if two substances differ considerably in their solubility in one and the same liquid they may be separated by treatment with successive small quantities of the liquid, which removes the more soluble compound but leaves the greater part of the other undissolved. The following is a list of the solvents commonly employed, with indications as to their general properties.

Water dissolves many salts and acids; inorganic and organic alkalis and their salts; carbohydrates, gums, and other highly oxidised carbon compounds which are not readily soluble in alcohol, ether, &c. On the other hand, it does not dissolve the carbonates, phosphates, oxalates, and certain other salts of the heavier metals. Very many organic substances are insoluble in this liquid. It decomposes the halogen compounds of the acid radicles and certain other compounds, and converts many normal metallic salts into basic salts, part of the acid passing into solution in the free state.

Dilute acids will dissolve many salts, and also some organic substances which are insoluble in water.

Alcohol dissolves many salts, caustic alkalis, hydrocarbons, fatty acids, resins, and a very large number of carbon compounds. It reacts with many haloid substitution derivatives, and hence is not a suitable solvent for this class of compounds.

Ether dissolves a few salts, and is an excellent solvent for hydrocarbons, fats, resins, alkaloïds, and almost all organic compounds which are insoluble in water. It reacts with very few substances, and boils at a low temperature, so that it can readily be distilled off and the dissolved substance recovered.

Benzene dissolves iodine, sulphur, phosphorus, oils, fats, wax, camphor, resins, caoutchouc, gutta-percha, &c., and is especially useful as a solvent for haloid derivatives, on which it has no action.

Carbon bisulphide shares with ether the advantage of being readily volatile. It should always be purified from dissolved sulphur before being used. The best plan is to mix it with a small quantity of white wax and then distil off the bisulphide on a water-bath. It dissolves sulphur, phosphorus, iodine, fats, essential oils, resins, caoutchouc, &c.; but its solvent powers are comparatively limited, and almost all salts

and very many carbon compounds are insoluble in it.

Light petroleum consists of the lower boiling hydrocarbons of the paraffin series. It occurs in commerce in several varieties under different names. *Petroleum ether* boils at  $50^{\circ}$ – $60^{\circ}$ ; *petroleum benzene* at  $70^{\circ}$ – $90^{\circ}$ ; *ligroin* at  $90^{\circ}$ – $120^{\circ}$ . They are excellent solvents for oils and fats, but dissolve very few other compounds.

Chloroform readily dissolves oils, fats, and similar substances, and is especially useful as a solvent for alkaloids.

The treatment of a solid with a volatile solvent must be conducted in a special apparatus, especially if the liquid is to be heated. Various forms of apparatus have been devised for this purpose, but there is none more efficient than that of Soxhlet (D. P. J. 232, p. 461). It consists of a short wide test tube, open at the top but closed at the bottom, to which is sealed a narrower tube which can be fitted into a small weighed flask by means of a cork. Communication between the two tubes is made by means of (1) a narrow side tube which opens into the



FIG. 5.

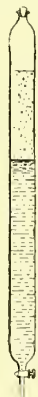


FIG. 6.

bottom of the wider upper tube, forms a siphon, and descends through the lower tube nearly to the bottom of the flask; and (2) a wider side tube which enters the upper tube near the top and the lower tube near the junction (fig. 5). A weighed quantity of the substance to be treated is placed in a cylinder of filter paper open at the top, and introduced into the upper tube, or the bottom of the tube is packed with purified cotton-wool, and the substance is placed upon this. A quantity of the solvent rather more than sufficient to fill the upper tube to the level of the bend in the siphon, is placed in the flask and heated to boiling by means of a water-bath. The upper tube is attached to a reflux condenser, care being taken that the condensed liquid falls directly into the cylinder containing the substance. The vapour passes up the wide side tube, is condensed, falls upon the substance, and filters through the paper or cotton-wool. As soon as the liquid rises to the bend of the siphon, the latter draws off the clear solution into the flask, and the liquid is again volatilised whilst the dissolved matter remains in the flask. The process goes on automatically, and the substance can be

extracted many times with a small quantity of liquid. When extraction is complete, the flask is connected with an ordinary condenser, the liquid is distilled off, and the residue dried and weighed if necessary.

A convenient apparatus for treatment with solvents in dishes has been described by A. W. Blyth (C. J. Trans. 1880, 140).

The older plan of allowing the substance to remain in contact with the solvent for a long time in a cylinder or other closed vessel is much less efficient.

In many cases substances in solution can be removed and separated by agitating the liquid with some non-miscible solvent. The alkaloids and many amines can be removed from aqueous solutions by means of ether, whilst metallic salts are left; fatty substances can be removed from liquids by means of petroleum ether, and so on. Extractions of this kind are best made in a separator consisting of a somewhat wide tube contracted at one end, which is fitted with a cork or stopper, whilst the other end is drawn out into a narrow tube provided either with a stopcock or an indiarubber tube and a pinch-cock (fig. 6). The liquid and the solvent can be completely mixed by agitation, and after they have separated the lower layer can be drawn off. If it is required to remove the supernatant liquid in this or any similar case, a somewhat narrow tube is bent twice at right angles, and one limb is fitted by means of a cork into a distilling or other flask which is connected with an aspirator, whilst the other limb of the tube is placed in the liquid. When the aspirator is set in action, the liquid is drawn over into the flask, from which it can be distilled. With care a very accurate separation can be made, and the tube is readily rinsed by drawing some of the fresh solvent through it.

The microscope is of the greatest service in ascertaining whether a substance is a single compound or a mixture, and a microscopic examination of the various products obtained in the course of a proximate analysis affords valuable information as to the extent to which separation has been effected.

#### Qualitative analysis.

The qualitative detection of substances is based upon the fact that almost every element or acid radicle will, under suitable conditions, yield a precipitate or reaction which, *under those conditions*, is characteristic, and enables us to distinguish it from everything else. With scarcely any exceptions the reactions of the metals and acid radicles are independent of the acids or metals with which they are respectively combined. The tests may be applied to the substance in solution, in which case they are known as *wet reactions*; or the solid substance may be subjected to the action of different solid reagents, usually at a high temperature, and these are known as *dry reactions*.

In framing a systematic scheme for the qualitative examination of a substance, advantage is first taken of certain similarities between the elements or radicles which enable us to divide them into a limited number of groups, and the individual members of these groups are afterwards separated by utilising the differences be-

tween the properties of their respective compounds.

The metals are divided into six groups according to their behaviour with the following reagents, which must be applied in the order given: (1) Metals precipitated as chlorides by hydrochloric acid. (2) Metals precipitated as sulphides by hydrogen sulphide in an acid solution. (3) Metals precipitated as hydroxides by ammonia in presence of ammonium chloride. (4) Metals precipitated as sulphides by ammonium sulphide in an alkaline solution. (5) Metals precipitated as carbonates by ammonium carbonate in presence of ammonia. (6) Metals not precipitated by these reagents.

In the case of acid radicals the division into groups is by no means so sharp, but barium chloride, calcium chloride, silver nitrate, and ferric chloride give reactions with a large number of acids, and can to a certain extent be utilised as group reagents.

The course to be adopted in making a qualitative analysis will depend very largely on circumstances. When the approximate composition of a substance is known, or when it is simply desired to prove the presence or absence of particular substances, the systematic scheme may be shortened very considerably. If, however, the composition of the substance is entirely unknown it is just as important to prove decisively that certain elements are absent as to prove that others are present. In all cases a preliminary examination of the substance should be made in the dry way, and if the substance is in solution a portion should be evaporated to dryness. The reactions of several substances in the dry way are interfered with and rendered inconclusive by the presence of certain other substances; but nevertheless an examination of this kind gives much information in a short time.

#### Examination in the Dry Way.

The most convenient source of heat for this purpose is the ordinary Bunsen burner. Considerable care is required in performing the experiments, and only small quantities of the substance must be operated upon. The Bunsen lamp consists of a metal tube at the bottom of which coal gas enters by means of a jet, the lower part of the tube being pierced with holes through which air is drawn and mixes with the coal-gas. The mixture of 1 volume of coal-gas with about  $2\frac{1}{2}$  volumes of air, which is thus produced, burns at the top of the tube with a non-luminous flame. When the supply of gas is turned low, it is necessary also to reduce the air supply by partially closing the holes at the bottom of the tube by means of a regulator. The upper part of the tube carries a gallery and cone to protect the flame from draughts.

The flame consists essentially of an inner dark zone containing unburnt gas mixed with air, and an outer zone or flame mantle in which combustion becomes complete. If the air holes are partially closed, a luminous cone appears at the top of the inner zone. Bunsen has shown, however, that several distinct zones exist, each of which can be utilised for producing particular reactions. The most useful of these are  $\alpha$ , a comparatively cold zone at the base of the flame, which serves for the volatilisation of

salts in order to obtain flame colourations; the lower reducing flame  $\delta$  about one quarter of the way up and close to the edge of the dark zone;  $\eta$ , the upper and more powerful reducing flame at the top of the dark zone, obtained by closing the air holes until the tip of the inner zone just becomes luminous;  $\beta$ , the zone of fusion or highest temperature, at about one-third

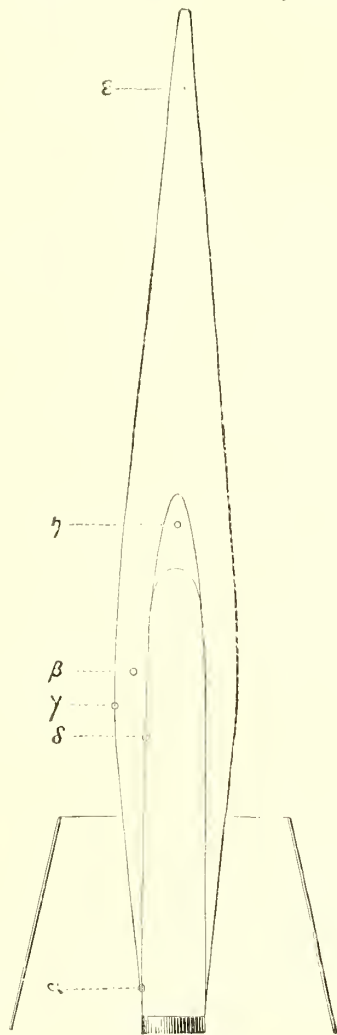


FIG. 7.

the height of the flame and half way between the inner zone and the flame mantle;  $\eta$ , the lower and hotter oxidising flame at the edge just below the zone of fusion; and  $\epsilon$ , the upper oxidising flame at the extreme tip of the flame.

Instead of the Bunsen lamp, the flame obtained by means of a blowpipe may be used. A mouth blowpipe consists of a metal tube provided at one end with a mouthpiece, the other end fitting into a small metal box which serves to condense and retain the moisture of the breath.



From the side of this box a second shorter and narrower tube projects at right angles to the first, and is provided with a nozzle or jet of brass or, better, of platinum. For general work the diameter of the bore of the jet should be 0.4 mm. In Black's blowpipe the larger tube is conical, the lower and wider end serving the

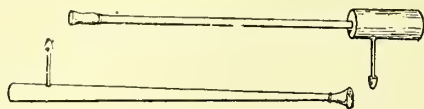


FIG. 8.

same purpose as the box in the form just described. The art of keeping up a continuous blast of air through the blowpipe can only be acquired by practice. The necessary pressure is produced by distending the cheeks, breathing being carried on through the nostrils, whilst communication between the nostrils and the mouth is cut off by the pressure of the tongue against the palate. A convenient form of hand-blower for blowpipe work has been devised by Fletcher.

A good flame for blowpipe work is obtained by dropping into the tube of an ordinary Bunsen burner a brass tube, the lower end of which descends to the bottom of the burner and cuts off the supply of air, whilst the upper end is flattened and cut off at an angle. The flame should be much smaller than when the burner is used in the ordinary way. Coal-gas usually contains more or less sulphur and consequently cannot be used when testing for this element.

A thick stearin candle answers well; but nothing is better than a lamp consisting of a low and somewhat wide cylindrical metal vessel, open at the top, with a somewhat broad and flat wick-holder attached to the side. The fuel used is solid paraffin, which is kept in a melted condition by the heat of the blowpipe flame, the wick being so arranged that the flame passes over the top of the paraffin. A metal cover protects the lamp from dust when not in use.

The nozzle of the blowpipe is introduced a short distance into the lamp flame at a short distance above the wick, and when the blast is produced the flame is deflected horizontally, becomes long and narrow, and is seen to consist of two parts, viz., an *outer* or *oxidising* flame, at the tip of which there is an excess of oxygen



FIG. 9.

heated to a high temperature, and an *inner* or *reducing* flame, which contains carbonic oxide and hydrocarbons heated to a high temperature. If the blowpipe is held just at the edge of the flame and a moderate blast is used, a broader reducing flame can be obtained, which has a luminous tip containing solid particles of carbon.

Other special apparatus required is a small pair of forceps with platinum points; short pieces of thin platinum wire; charcoal from some fine-grained compact wood; glass tubes about

3 mm. internal diameter, and 60-80 mm. long, closed at one end; and glass tubes of similar diameter 100-120 mm. long, open at both ends and bent slightly in the middle. The reagents used are borax, microcosmic salt ( $\text{NH}_4\text{NaHPO}_4$ ), potassium cyanide, sodium carbonate, potassium nitrate, cobalt nitrate solution, and potassium hydrogen sulphate.

The usual operations are as follows:—

(1) *Heating in closed tube.* The sides of the tube must be clean and perfectly dry; after introduction of the substance they may be cleaned by means of a roll of filter paper.

(2) *Heating in an open tube,* the tube being inclined in order to promote a current of air through it.

(3) *Heating on platinum wire* in order to obtain a flame colouration. The wire is cleaned by repeated dipping into hydrochloric acid and heating in the flame until it imparts no colour. A small quantity of the substance is taken on the end of the clean wire and introduced into the edge of the blowpipe flame just beyond the top of the inner flame, or into zone  $\alpha$  of the Bunsen flame. A colouration is only obtained if the metal is in the form of some volatile compound, and since the chlorides are amongst the most volatile salts, the substance should be moistened with hydrochloric acid. An excellent plan is to mix the substance with a small quantity of precipitated silver chloride, which is kept in a paste with water, and heat the mixture on a thin iron wire. Silver imparts no colour to the flame, but chlorine is given off gradually, and converts the other metals into chlorides. A mixture of several substances may be made to show successively their individual flame colourations by first heating in a comparatively cold part of the flame until the most volatile is expelled, then moving to a somewhat hotter zone, and so on.

(4) *Heating on charcoal* to obtain reduced metal or a film of oxide. The substance, mixed with three times its weight of dry sodium carbonate or of a mixture of 2 parts sodium carbonate and 1 part potassium cyanide, is placed in a small shallow hole scooped out in charcoal, and heated in a reducing flame. The metallic bead obtained is examined as to colour, malleability, solubility, &c. Many metals yield films of oxide which coat the charcoal at a greater or less distance from the flame, and the colour and appearance of which is more or less characteristic. These and similar films are best seen when the charcoal is supported on an aluminium plate (Ross). A piece of sheet aluminium 12 cm. by 5 cm. is bent at right angles at a distance of 2 cm. from one end, thus forming a ledge on which a small flat piece of charcoal is placed, the plate being held so that the surface rises vertically behind the ledge. Volatile oxides &c. condense on the metallic surface (*v. Hutchings*, C. N. 36, 208, 217).

In order to obtain reduced metals with the Bunsen flame, a match-stick is smeared with ordinary sodium carbonate (washing soda) which has been melted by holding it in the flame, and the wood thus prepared is carbonised by heating it in the flame. A small quantity of the substance is mixed in the palm of the hand with a small quantity of the fused washing soda and the mixture is carefully placed on the charcoal

splint, which is then heated in the lower or upper reducing flame. When reduction is complete the match is allowed to cool inside the dark zone, and is then withdrawn, crushed in a mortar, and the lighter particles of charcoal removed by levigation with water, the heavy metallic particles being left.

By means of the Bunsen flame reduced metals and their oxides can be obtained in the form of films on a porcelain surface. The substance is supported on a long slender piece of asbestos, and heated in the tip of a small oxidising or reducing flame, a small evaporating dish containing cold water being held momentarily just above the asbestos (*v. Bunsen's 'Flammen-reactionen,' Heidelberg, 1880*).

(5) *Heating with borax or microcosmic salt.*—A small loop is made at the end of a platinum wire, and some borax or microcosmic salt is taken up and heated in the flame until it is perfectly fused. The bead when cold must be quite transparent and colourless, otherwise it must be remelted, shaken off, and a fresh bead made. A small quantity of the substance is taken on the bead and heated first in the oxidising flame (O.F.) and then, after it has been examined, in the inner or reducing flame (I.F.). The colour of the bead should be observed both hot and cold. If too much substance is taken the bead becomes opaque, and the colour cannot be distinguished.

(6) Certain *infusible* substances, when moistened with cobalt nitrate solution and strongly heated, acquire characteristic colours.

The following results may be obtained:—

(1) *In closed tube:*—

(a) It carbonises, with or without evolution of empyreumatic vapours = *organic compounds*.

(b) Water is evolved and condenses in the cold part of the tube; neutral reaction = *hydrated salts, hydroxides*; acid reaction = *acid salts*; alkaline reaction = *ammonium compounds*.

(c) Fuses without change of colour = *alkaline salts; hydrated salts*.

(d) Fuses and changes colour: yellow hot, dark yellow cold = *bismuth oxide*; yellow hot, red cold = *lead oxide*.

(e) No fusion, but change of colour: dark yellow hot, pale yellow cold = *stannic oxide*; yellow hot, white cold = *zinc oxide*; black hot, reddish-brown cold = *ferric oxide*; black hot, bright red cold = *mercuric oxide*.

(f) Gas is evolved: oxygen = *chlorates, iodates, &c., peroxides*; carbon dioxide = *carbonates, oxalates*; carbon monoxide (burns with blue flame) = *formates, oxalates*; sulphur dioxide = *acid sulphites, sulphates of heavy metals*; cyanogen = *cyanides*; ammonia = *ammonium salts*: orange-brown vapours = *nitrates, nitrites, bromides*; violet vapours = *iodides*.

(g) A sublimate is formed: black or reddish-black = *selenium, mercuric sulphide*; reddish-yellow = *arsenic sulphide*; yellow = *sulphur, sulphides*; white = *ammonium salts, mercury salts, volatile organic acids, antimony trioxide* (needles); arsenic trioxide (octahedra); metallic mirror = *arsenic*; grey metallic globules = *mercury*.

(2) *In open tube* much the same results as in closed tube. Sulphides burn and give off sulphur dioxide; arsenic sublimes as oxide and not as metal; selenium and its compounds evolve a

pungent odour of horse-radish, and give a grey or reddish sublimate.

(3) *Flame colouration:*—yellow = *sodium*; orange red = *calcium*; crimson = *strontium, lithium*; lavender = *potassium*; apple-green = *barium*; bright green = *thallium, copper, boric acid*; pale blue = *lead, antimony*; deep blue, becoming green = *copper (haloid salts)*; deep blue = *selenium*.

(4) *On charcoal.*—White malleable bead = *silver, tin, lead*; red malleable bead = *copper*; grey magnetic powder = *iron, nickel, cobalt*; brittle bead = *antimony, bismuth*.

Incrustations on charcoal: white = *antimony*; orange-yellow hot, pale yellow cold = *bismuth*; pale yellow hot, deeper yellow cold, with white edge = *lead*; white, very volatile = *arsenic*; yellow hot, white cold = *zinc*; reddish-brown or orange-yellow cold = *cadmium*.

(5) *In borax bead:*—

Inner flame		Outer flame		Metal
Hot	Cold	Hot	Cold	
Green	Bottle-green	Yellow	Paler	<i>Iron</i>
Green	Green	Yellow	Green	<i>Chromium</i>
Green	Bottle-green	Yellow	Pale yellow	<i>Uranium</i>
Colourless	Colourless	Amethyst	Amethyst	<i>Manganese</i>
Blue	Blue	Blue	Blue	<i>Cobalt</i>
Grey	Grey	Violet	Reddish-brown	<i>Nickel</i>
Brownish	Emerald green	Yellow	Greenish-yellow	<i>Vanadium</i>
Colourless	Brown	Green	Bluish-green	<i>Copper</i>

(6) *With cobalt nitrate:*—blue = *aluminium* (some phosphates, silicates, and borates); green = *zinc, titanium*; pale red = *magnesium*.

#### Examination in the Wet Way.

The preparation of the solution requires some attention. If the substance is a metal, treat at once with moderately strong nitric acid. Tin and antimony form oxides which to a great extent remain undissolved; other metals (with the exception of gold and the platinum metals, which are not attacked) are converted into nitrates, which dissolve at once or on diluting.

If the substance is not a metal, it is first treated with hot water, and if anything is dissolved (which is ascertained by evaporating a few drops on platinum foil), the substance is boiled two or three times with fresh quantities of water. Any residue which may be left is treated with dilute hydrochloric acid, and afterwards, if necessary, with the concentrated acid. Care must be taken to observe if any gas is given off—e.g., carbon dioxide (effervescence), from carbonates; sulphur dioxide, from sulphites or thiosulphates; chlorine, from peroxides or hypochlorites; hydrocyanic acid, from cyanides; hydrogen sulphide, from sulphides. Many chlorides are insoluble in the strong acid, and hence the solution must be diluted before filtering. Any metals of Group I. will be converted into insoluble chlorides.

Any residue insoluble in hydrochloric or nitric acids must be treated with aqua regia (a mixture of hydrochloric acid 3 parts, and nitric acid 1 part) and the excess of acid expelled by evaporation. Substances which are insoluble in aqua regia are examined in the dry way, or converted into soluble compounds. They may contain stannic oxide; crystallised or strongly ignited aluminium or chromium oxides; silica



or silicates; barium sulphate; silver chloride, bromide or iodide; antimony trioxide; fluorides.

Silicates, insoluble sulphates, silver compounds, &c., are fused with three or four times their weight of a mixture of potassium and sodium carbonates in equal proportions. A porcelain crucible must be used for silver or lead compounds. The fused mass, after cooling, is treated with water, which dissolves out the acids as alkaline salts; the residue is then dissolved in acids.

Insoluble compound cyanides are decomposed by heating with strong sulphuric acid; also by treatment with potassium or sodium hydroxide, which dissolves the acids as alkaline salts, and leaves the metals as hydroxides which are soluble in hydrochloric acid.

When both aqueous and acid solutions have been obtained from the same substance the analyst must use his own judgment as to whether they may be mixed or should be analysed separately. The latter course sometimes gives information as to the distribution of the acids and bases in the original substance. If the first course is adopted, it must be borne in mind that the hydrochloric acid solution may precipitate metals of Group I. from an aqueous or nitric acid solution.

#### Systematic method of examination in the wet way.

The formation of a precipitate at the proper stage in the systematic separation is not sufficient proof of the presence of a particular substance; some characteristic confirmatory test should always be applied. In the course of the analysis, observe carefully the colour of the solutions at different stages in the operation. Unnecessary excess of the group or other reagents should be avoided, but the filtrate from a group should always be tested to make sure that precipitation is complete. Many tests succeed only when the proper proportion of the reagent is added, and it should be a rule always to add the reagents very gradually. Group precipitates and all other precipitates which have to be subjected to the action of reagents should be carefully washed, but in qualitative analysis it is not as a rule desirable that the washings should mix with the filtrate.

Note the reaction of the solution.

Test a small portion of the solution for ammonia by heating with sodium hydroxide.

GROUP I.—Add hydrochloric acid to acid reaction. If no precipitate, pass on; if a precipitate is formed, add more acid to ensure complete precipitation or re-solution of the precipitate. *Silver, mercury* (mercurous), *lead, thallium*, are precipitated as chlorides; *tungsten* as tungstic acid.

If the original solution is alkaline the precipitate by hydrochloric acid may consist of metallic sulphides which had been dissolved in an alkaline sulphide. The precipitate will be yellow or orange, and must be examined like the subdivision of Group II. Under these circumstances none of the ordinary metals of the first group except tungsten, and very few of the others except those of the fifth and sixth groups, can be present.

The precipitate may also consist of insoluble silver salts which had been dissolved in an alkaline cyanide or thiosulphate. In this case it must be dried and fused with the alkaline carbonates like an insoluble compound.

GROUP II.—If the filtrate from Group I. contains nitric acid or nitrates it must be evaporated to dryness two or three times with small quantities of strong hydrochloric acid in order to remove these compounds, and the residue redissolved in dilute hydrochloric acid. The solution, which should be moderately dilute and not contain too much free acid, is gently heated, and saturated with hydrogen sulphide. *Mercury* (mercuric), *lead, bismuth, copper, cadmium, arsenic, antimony, tin, gold, platinum* (and the *platinum metals*), *molybdenum, and selenium* are precipitated as sulphides. Prolonged treatment with hydrogen sulphide is required to precipitate molybdenum and the platinum metals.

GROUP III.—The filtrate from Group II. is boiled to expel all hydrogen sulphide, and heated with nitric acid to peroxidise the iron. If organic matter or oxalates are present, it is evaporated to dryness, heated until they are decomposed, and the residue dissolved in dilute hydrochloric acid. Any insoluble residue may be silica or barium sulphate.

The solution is then mixed with ammonium chloride and a slight excess of ammonia, and heated to boiling. *Aluminium, iron, chromium, and beryllium* are precipitated as hydroxides; *uranium and cerium* as salts or basic salts.

GROUP IV.—The filtrate from Group III. is heated to boiling, and mixed gradually with a slight excess of ammonium sulphide. *Zinc, manganese, cobalt, and nickel* are precipitated as sulphides. Nickel sulphide is somewhat soluble in excess of the precipitant.

If the filtrate is brown it is *slightly* acidified with hydrochloric acid; *vanadium* sulphide, (and nickel) is precipitated.

GROUP V.—The filtrate from Group IV. is mixed with ammonia and ammonium carbonate. *Calcium, barium, and strontium* are thrown down as carbonates.

GROUP VI.—The filtrate from Group V. contains *magnesium, sodium, and potassium* (lithium *casium, rubidium*).

The group precipitates are examined by the following methods:—

GROUP I.—The group precipitate is boiled with two or three successive quantities of water, filtered, and the filtrate mixed with dilute sulphuric acid; a white precipitate ( $\text{PbSO}_4$ ) indicates *lead*. The portion insoluble in water is treated with strong ammonia and filtered; a black residue ( $\text{NH}_4\text{HgCl}$ ) indicates *mercury*. The ammoniacal filtrate is acidified with nitric acid; a white precipitate ( $\text{AgCl}$ ) indicates *silver*.

GROUP II.—The precipitate is washed with water containing hydrogen sulphide, warmed with yellow ammonium sulphide and filtered (A). This treatment is repeated once or twice. The insoluble portion is treated with warm dilute nitric acid, and filtered (B). The residue in, soluble in nitric acid is dissolved in aqua regia, excess of acid expelled, and stannous chloride added; white precipitate ( $\text{Hg}_2\text{Cl}_2$ ) changing to grey ( $\text{Hg}$ ) indicates *mercury*.



(A) The ammonium sulphide solution is acidified with hydrochloric acid, and filtered. The precipitate is gently warmed with a strong solution of ammonium carbonate, again filtered, and the filtrate acidified with hydrochloric acid; a yellow precipitate = *arsenic* (confirm by dry tests). The portion insoluble in ammonium carbonate is dissolved in strong hydrochloric acid, boiled to expel hydrogen sulphide, diluted, and platinum foil and a piece of zinc free from tin are introduced. A black stain on the platinum = *antimony*. After a short time the zinc is removed, dissolved in hydrochloric acid, and mercuric chloride added; a white precipitate becoming grey = *tin*.

(B) The nitric acid solution is evaporated to a small bulk with some sulphuric acid, diluted, and filtered. A white residue ( $\text{PbSO}_4$ ) indicates *lead*. The filtrate is mixed with ammonia in slight excess, and again filtered; a white precipitate ( $\text{Bi}(\text{HO})_3$ ) = *bismuth* (confirm by dissolving in a small quantity of hydrochloric acid and pouring into a large quantity of water). The ammoniacal filtrate is blue = *copper*. Add potassium cyanide until the solution is colourless, and then hydrogen sulphide; a yellow precipitate ( $\text{CdS}$ ) = *cadmium*.

GROUP III.—Dry the precipitate and fuse on platinum with 2 parts pure sodium carbonate and 1 part potassium nitrate. If the fused mass has a green colour, *manganese* is present. Dissolve in water (if green add a few drops of alcohol) and filter. Dissolve the residue ( $\text{Fe}_2\text{O}_3$ ) in hydrochloric acid, and add potassium ferrocyanide; dark-blue precipitate = *iron* (ascertain state of oxidation from original solution). The aqueous solution is divided into two parts, one is heated with excess of ammonium chloride; a white precipitate ( $\text{Al}_2(\text{HO})_6$ ) indicates *aluminium*; the other is acidified with acetic acid and tested with lead acetate; a yellow precipitate ( $\text{PbCrO}_4$ ) = *chromium* (ascertain degree of oxidation in original solution).

If the original solution was acid this group precipitate may contain metallic phosphates precipitated as such on neutralising with ammonia. In this case dissolve a small portion of the precipitate in nitric acid, and examine for phosphoric acid by the molybdc test. If phosphates are absent, proceed as just described; if present, proceed as follows:—Examine one-third of the precipitate by the preceding method. Dissolve the remaining two-thirds in hydrochloric acid, add sodium acetate in tolerably large excess, and then ferric chloride until no more precipitate forms and the solution acquires a deep-red colour. Now boil, and filter whilst hot. Under these conditions the ferric chloride precipitates the phosphoric acid, and the metals remain in solution as chlorides. Examine the filtrate, which should be quite colourless, for metals of Groups IV. and V., and for magnesium.

GROUP IV.—Wash well with water containing hydrogen sulphide, and treat with cold dilute hydrochloric acid (1:20). Filter, boil the filtrate to expel all hydrogen sulphide, and add potash or soda in excess; a white precipitate ( $\text{Mn}(\text{HO})_2$ ) becoming brown on exposure to air = *manganese*. To the filtrate from this precipitate add ammonium sulphide; a white precipitate ( $\text{ZnS}$ ) indicates *zinc*.

The portion insoluble in cold dilute hydrochloric acid is first tested for cobalt by the borax bead, and then dissolved in strong hydrochloric acid with the aid of a few crystals of potassium chlorate, or in aqua regia, and concentrated to expel excess of acid. Potash or soda is then added to alkaline reaction and potassium cyanide until the precipitate dissolves. The solution is now boiled for some time in a dish with free exposure to air, then mixed with sodium hypochlorite solution in moderately large quantity and boiled again; a black precipitate ( $\text{Ni}_3\text{O}_2 \cdot x\text{H}_2\text{O}$ ) indicates *nickel*. If cobalt has not been found by the borax bead, acidify the filtrate with hydrochloric acid, evaporate to complete dryness, heat the residue for some time with excess of strong sulphuric acid, dilute with water, neutralise with ammonia, add ammonium sulphide, and test with a borax bead any precipitate which may form.

GROUP V.—Dissolve the washed precipitate in hydrochloric acid, add ammonium sulphate in considerable quantity, boil and filter. Neutralise the filtrate with ammonia, and add ammonium oxalate; a white precipitate ( $\text{CaC}_2\text{O}_4$ ) = *calcium*. The precipitate by ammonium sulphate is boiled with a solution of potassium carbonate 1 part and potassium sulphate 3 parts, filtered hot, and the well-washed precipitate treated with dilute hydrochloric acid. Any insoluble residue is tested in the flame for *barium*. The hydrochloric acid solution is tested in the flame, and also mixed with calcium sulphate; white precipitate ( $\text{SrSO}_4$ ) forming slowly = *strontium*.

GROUP VI.—Part of the filtrate from Group V. is mixed with ammonia and sodium phosphate; white precipitate ( $\text{NH}_4\text{MgPO}_4$ ) = *magnesium*.

The remainder is evaporated to dryness, heated to expel ammonium salts, dissolved in water, mixed with oxalic acid, again evaporated to dryness and heated to expel excess of the acid. Dissolve in water and filter; test one part of the solution by flame test and potassium met-antimoniate for *sodium*; the other by flame test and platonic chloride for *potassium*.

#### Examination for acids.

(A) *Preliminary*. Mix the solid substance with three or four times its volume of strong sulphuric acid and heat, taking care that the acid does not boil.

No action—*sulphate, phosphate, borate, silicate, arsenate, arsenite*.

Gas is evolved:—

a. Colourless.

Fuming and acid, does not etch; *chloride*.

Fuming, acid, and etches glass; *fluoride*.

Smell of vinegar; *acetate*.

Carbon dioxide, turns lime-water milky; *carbonate*.

Carbon monoxide, burns with blue flame; *formate, ferrocyanide*.

Carbon dioxide and monoxide; *oxalate*.

Hydrocyanic acid; *cyanide*.

Sulphur dioxide, no sulphur; *sulphite*.

Sulphur dioxide, and sulphur precipitated; *thiosulphate*.

Hydrogen sulphide; *sulphide, iodide*.

β. Coloured.

Violet vapours of iodine; *iodide*.

Orange vapours of bromine; *bromide*.

Reddish-brown nitrogen oxides; *nitrite* (*nitrate*).

Yellow and explosive chlorine oxide; *chlorate*.

Substance carbonises and evolves carbon dioxide and monoxide and sulphur dioxide; *tartrate, citrate, malate*.

**Group reagents.**—Before testing a solution for acids, boil with excess of pure sodium carbonate to remove heavy metals, filter, and carefully neutralise with nitric acid.

(B) *Barium chloride* in neutral solution yields (α) a white precipitate, insoluble in hydrochloric acid = *sulphate, hydrofluosilicate*; (β) a white precipitate, soluble in hydrochloric acid = *sulphite, carbonate, phosphate, oxalate, borate, fluoride, silicate, tartrate*; (γ) a yellow precipitate = *chromate*.

(C) To a portion of the neutral solution add *calcium chloride* in excess, allow to stand for some time with occasional shaking, and filter. A white precipitate (α) insoluble in acetic acid = *oxalate* (*sulphate* in strong solutions). (β) soluble in acetic acid = *phosphate, borate*, and other acids precipitated by barium chloride.

Calcium *tartrate* after washing is soluble in potash, and is re-precipitated on diluting and boiling.

The filtrate from the precipitate in the cold is boiled for some time and filtered hot; a white precipitate = *citrate* (*malate* in strong solutions). The filtrate from this precipitate is allowed to cool and is mixed with excess of alcohol; a white precipitate = *succinate, malate*.

(D) *Silver nitrate* in neutral solution yields:—

(α) A precipitate soluble in nitric acid.

(1) White = *oxalate, borate, tartrate, benzoate, &c.*

(2) Yellow = *phosphate, arsenite*.

(3) Brick-red = *arsenate*.

(4) Dark-red = *chromate* (soluble only in hot strong nitric acid).

(β) A precipitate insoluble in nitric acid.

Soluble in ammonia: White = *chloride* (*hypochlorite*), *cyanide, thiocyanate*; yellowish-white = *bromide*; orange-red = *ferrieyanide*.

Insoluble in ammonia: White = *ferroeyanide*; yellow = *iodide*; black = *sulphide*.

(E) *Ferric chloride* in neutral solutions yields:—

(α) A colouration: blood-red = *acetate, formate* (precipitate on boiling), *thiocyanate* (no precipitate on boiling); violet = *salicylate, thiosulphate* (fugitive); bluish-black = *tanmate, gallate*; greenish-brown = *ferrieyanide* (dark-blue precipitate on adding stannous chloride).

(β) A precipitate: buff = *benzoate, carbonate*; reddish-brown = *succinate*; white = *phosphate*; black = *sulphide*; bluish- or greenish-black = *tanmates, gallates*.

**Sulphur acids.** Detect *sulphates* by barium chloride, and *sulphides* by lead acetate, &c. Make part of the solution slightly alkaline with potash, add zinc sulphate in considerable excess, and filter. Test one part of the filtrate for *thiosulphate* by means of hydrochloric acid; to the other part add acetic acid till faintly acid, sodium nitroprusside in small quantity,

and potassium ferroeyanide; a pink precipitate indicates a *sulphite*.

**Chlorine, bromine, and iodine.** Place the substance in a small flask connected with a small bulb U-tube containing a little starch paste and placed in a beaker of water. Add water and ferric sulphate solution to the substance in the flask, and heat to boiling. If iodine is present, the starch paste becomes blue. Remove the cork, boil with fresh additions of ferric sulphate till all iodine is expelled. Now add a few crystals of potassium permanganate, connect with a bulb tube containing chloroform, and again boil. If bromine is present, the chloroform is coloured brown. Boil with addition of more permanganate until all bromine is expelled, filter and test filtrate for chlorine.

After iodine has been detected by means of nitrogen oxides in sulphuric acid, evaporate part of the solution to dryness with sodium carbonate, fuse with ten times its weight of potassium dichromate till all iodine is expelled, place in a small dry retort, and heat with strong sulphuric acid. Part of the distillate is agitated with water and carbon bisulphide; if bromine is present, the latter becomes orange-red. The remainder of the distillate is neutralised with ammonia, and tested for chromic acid by acidifying with acetic acid and adding lead acetate. The presence of chromic acid indicates the presence of chlorine in the original substance.

*Other acids* must be detected by special tests. Iodine, and ferroeyanides and ferrieyanides must be removed before testing for nitrates.

To remove *iodine, ferroeyanide, ferrieyanide, and thiocyanic acids*, add excess of a mixture of cupric and ferrous sulphates, and filter. To remove excess of copper and iron (which is not always necessary) heat to boiling, add slight excess of pure potash or soda, and filter.

To remove *bromine and iodine*, acidify with dilute sulphuric acid, and boil with successive additions of potassium permanganate until the liquid has a faint permanent pink tinge; filter.

To remove *hypochlorous and nitrous acids*, acidify with dilute sulphuric acid, and boil. Nitrous acid can also be decomposed by boiling with a strong solution of ammonium chloride.

### SPECIAL REACTIONS.

In the following lists only the most characteristic and useful reactions have been given; negative reactions, and others not particularly characteristic, have, as a rule, been omitted.

### METALS.

The metals are arranged in the order of their occurrence in the systematic separation.

#### Silver.

On charcoal, brilliant-white malleable bead, soluble in nitric acid.

*Hydrochloric acid*, a white precipitate ( $\text{AgCl}$ ); insoluble in hot water and in nitric acid; soluble in ammonia and reprecipitated by nitric acid in excess. *Potassium chromate*, a dark-red precipitate ( $\text{AgCrO}_4$ ); soluble in hot concentrated nitric acid.

#### Lead.

On charcoal, malleable bead, soluble in nitric acid; oxide film yellow with white border.

*Hydrochloric acid*, a white precipitate ( $\text{PbCl}_2$ ), soluble in hot water, from which it crystallises on cooling; insoluble in ammonia. *Hydrogen sulphide*, a black precipitate ( $\text{PbS}$ ), insoluble in ammonium sulphide; soluble in nitric acid. *Sulphuric acid*, a white precipitate ( $\text{PbSO}_4$ ), soluble in hot dilute hydrochloric acid; insoluble in dilute sulphuric acid. *Potassium chromate*, yellow precipitate ( $\text{PbCrO}_4$ ), insoluble in acetic acid; soluble in potassium hydroxide.

#### **Thallium.**

*Flame colouration* intense green.

*Hydrochloric acid*, white precipitate ( $\text{TlCl}$ ), only slightly soluble in hot water. *Potassium iodide*, pale-yellow precipitate ( $\text{TlI}$ ), even in dilute solutions. *Sulphuric acid*, no precipitate (diff. f. Pb).

#### **Tungsten.**

*Microcosmic salt*, colourless in OF; blue in I.F., becoming blood-red on addition of  $\text{FeSO}_4$ .

*Hydrochloric acid*, a yellowish-white precipitate ( $\text{H}_2\text{WO}_4$ ), insoluble in excess of the dilute acid; soluble in the concentrated acid; fragments of zinc added to this solution produce a blue colouration. *Stannous chloride*, a yellow precipitate, which becomes blue if mixed with hydrochloric acid and heated.

#### **Mercury.**

Heated in closed tube most mercury salts sublime; heated with sodium carbonate, a sublimate of metallic mercury.

*Mercurous salts*. *Hydrochloric acid*, white precipitate ( $\text{Hg}_2\text{Cl}_2$ ), insoluble in hot water; insoluble in ammonia, but blackened ( $\text{NH}_2\text{Hg}_2\text{Cl}$ ). *Stannous chloride*, grey precipitate ( $\text{Hg}$ ). *Metallic copper*, becomes coated with mercury, which can be sublimed.

*Mercuric compounds*. *Hydrogen sulphide*, white precipitate, becoming red and then black ( $\text{HgS}$ ); insoluble in ammonium sulphide; insoluble in nitric acid; soluble in aqua regia. *Stannous chloride*, white precipitate ( $\text{Hg}_2\text{Cl}_2$ ), becoming grey ( $\text{Hg}$ ) with excess of the reagent. *Potassium iodide*, scarlet precipitate ( $\text{HgI}_2$ ), soluble in excess. *Metallic copper*, as mercurous salts.

#### **Bismuth.**

*On charcoal*, brittle bead; oxide incrustation orange-yellow when hot, lemon-yellow when cold.

*Hydrogen sulphide*, brown precipitate ( $\text{Bi}_2\text{S}_3$ ), insoluble in ammonium sulphide; soluble in nitric acid. *Ammonia*, white precipitate ( $\text{Bi}(\text{HO})_3$ ), soluble in hydrochloric acid. *Water* in large excess (with previous addition of ammonium chloride if chlorides are absent), white precipitate ( $\text{BiOCl}$ ), soluble in hydrochloric acid; insoluble in tartaric acid.

#### **Copper.**

*On charcoal*, red malleable metal. *Borax*, O.F. green hot, bluish-green cold; I.F. colourless hot, brown cold.

*Hydrogen sulphide*, black precipitate ( $\text{CuS}$ ), insoluble in ammonium sulphide, and in dilute sulphuric acid; soluble in nitric acid and in potassium cyanide. *Ammonia*, blue precipitate, soluble in excess to dark-blue solution. *Potassium ferrocyanide*, chocolate-brown precipitate, insoluble in dilute acids; in very dilute solutions colouration only.

#### **Cadmium.**

*On charcoal*, brown incrustation of oxide.

*Hydrogen sulphide*, yellow precipitate ( $\text{CdS}$ ), insoluble in ammonium sulphide and potassium cyanide; soluble in nitric acid and hot dilute sulphuric acid. *Ammonia*, white precipitate ( $\text{CdH}_2\text{O}_2$ ), readily soluble in excess. *Potash soda*, white precipitate ( $\text{CdH}_2\text{O}_2$ ) insoluble in excess.

#### **Tin.**

*On charcoal*, white malleable bead; incrustation of oxide, yellow hot, white cold.

*Stannous compounds*. *Hydrogen sulphide*, dark-brown precipitate ( $\text{SnS}$ ), soluble in yellow but not in colourless ammonium sulphide. *Mercuric chloride*, white precipitate ( $\text{Hg}_2\text{Cl}_2$ ), becoming grey ( $\text{Hg}$ ).

*Stannic compounds*. *Hydrogen sulphide*, yellow precipitate ( $\text{SnS}_2$ ), soluble in ammonium sulphide; insoluble in ammonium carbonate; soluble in concentrated hydrochloric acid. *Stannic chloride* boiled with copper becomes stannous chloride. When zinc and platinum are placed in the solution, no black stain on the platinum; crystals of tin on the zinc.

#### **Antimony.**

*On charcoal*, white incrustation of oxide.

*Hydrogen sulphide*, orange precipitate ( $\text{Sb}_2\text{S}_3$ ), soluble in ammonium sulphide and in concentrated hydrochloric acid; insoluble in ammonium carbonate. *Water* in excess (with ammonium chloride if chlorides are absent), white precipitate ( $\text{SbOCl}$ ), soluble in hydrochloric acid and in tartaric acid. *Zinc* and *platinum*, a black stain on the platinum ( $\text{Sb}$ ), soluble in nitric acid and in ammonium sulphide.

#### **Arsenic.**

*In open tube*, white sublimate ( $\text{As}_2\text{O}_3$ ) in microscopic octahedra and tetrahedra. *In closed tube*, with potassium cyanide and sodium carbonate, dark shining sublimate of metallic arsenic (diff. f. Sb).

*Hydrogen sulphide*, yellow precipitate, soluble in ammonium sulphide and in ammonium carbonate; insoluble in concentrated hydrochloric acid. *Metallic copper* boiled with the liquid after acidifying with hydrochloric acid is covered with a shining grey deposit ( $\text{As}_2\text{Cu}_3$ ), which, when heated in a tube, yields a sublimate of arsenious oxide (Reimsch's test).

*Arsenites*. *Ammonio-silver nitrate*, yellow precipitate ( $\text{Ag}_3\text{AsO}_3$ ), soluble in nitric acid and ammonia. *Ammonio-cupric sulphate*, bright-green precipitate ( $\text{CuHASO}_3$ ).

*Arsenates*. *Ammonio-silver nitrate*, brick-red precipitate ( $\text{Ag}_3\text{AsO}_4$ ), soluble in nitric acid and ammonia. *Ammonium chloride*, ammonia, and *magnesium sulphate*, white crystalline precipitate ( $\text{NH}_4\text{MgAsO}_4$ ).

When arsenic acid or arsenates are present they should be reduced by heating with sulphurous acid before applying hydrogen sulphide or Reimsch's test.

#### **Platinum.**

*Hydrogen sulphide*, brown precipitate ( $\text{PtS}$ ) on heating, soluble in ammonium sulphide. *Ammonium chloride* or *potassium chloride*, yellow crystalline precipitate ( $\text{M}_2\text{PtCl}_6$ ), less soluble in presence of alcohol.

#### **Palladium.**

*Hydrogen sulphide*, black precipitate ( $\text{PdS}$ ), insoluble in ammonium sulphide; soluble in



hot hydrochloric acid and in aqua regia. *Potassium iodide*, black precipitate ( $\text{PbI}_2$ ), somewhat soluble in excess. *Mercuric cyanide*, yellowish white, gelatinous precipitate ( $\text{PdCy}_2$ ), readily soluble in ammonia. *Ammonium chloride*, no precipitate (diff. from Pt). *Potassium chloride*, precipitate ( $2\text{KCl}.\text{PdCl}_2$ ) only in very concentrated solutions.

#### Iridium.

*Hydrogen sulphide*, decolourisation followed by brown precipitate ( $\text{Ir}_2\text{S}_3$ ), soluble in ammonium sulphide. *Potash*, a greenish colouration, which, on heating with exposure to air, changes slowly to azure blue (diff. from Pt). *Ammonium chloride* or *potassium chloride*, dark brown or red precipitate (double chloride), insoluble in a saturated solution of the precipitant. Both salts become olive green with potassium nitrite and other reducing agents, especially in hot solutions.

#### Gold.

*Hydrogen sulphide*, black precipitate ( $\text{Au}_2\text{S}_3$ ) in cold, brown precipitate ( $\text{Au}_2\text{S}$ ) in hot, solution; soluble in yellow ammonium sulphide. *Oxalic acid* or *ferrous sulphate*, brown or purple precipitate, yellow and lustrous when rubbed. *Stannous and stannic chlorides*, purplish precipitate, insoluble in hydrochloric acid.

#### Molybdenum.

*Borax bead*, O.F. yellowish, hot; colourless, cold; I.F. brown. *Microcosmic salt*, O.F. green, hot; pale-green, cold; I.F. green.

*Hydrogen sulphide*, brownish-black precipitate ( $\text{MoS}_3$ ) on heating, soluble in ammonium sulphide. *Sodium phosphate* in presence of nitric acid, yellow precipitate on heating, soluble in ammonia and in excess of the alkaline phosphate.

#### Selenium.

*On charcoal* in I.F., a pungent smell resembling horse-radish.

*Hydrogen sulphide*, yellow precipitate becoming dark on heating, soluble in ammonium sulphide. *Sulphurous acid* in presence of hydrochloric acid, a red precipitate which becomes grey on heating and is soluble in potassium cyanide. *Stannous chloride* and other reducing agents behave in a similar manner.

#### Aluminium.

*On platinum wire*, with cobalt nitrate, blue mass.

*Ammonia*, white gelatinous precipitate ( $\text{Al}_2\text{H}_2\text{O}_6$ ), insoluble in excess and in ammonium carbonate; soluble in acids. *Potash* or *soda*, white gelatinous precipitate ( $\text{Al}_2\text{H}_2\text{O}_6$ ), soluble in excess; reprecipitated on adding ammonium chloride and heating.

#### Chromium.

*Borax bead*, O.F. yellow, hot; green, cold; I.F. green. Fused with *potassium nitrate* and *sodium carbonate*, soluble yellow potassium chromate is formed.

**Chromic salts.** *Ammonia*, greenish or purplish precipitate ( $\text{Cr}_2\text{H}_2\text{O}_6$ ), soluble in acids; insoluble in ammonium carbonate. *Potash* or *soda*, green precipitate ( $\text{Cr}_2\text{H}_2\text{O}_6$ ), soluble in excess, but reprecipitated on boiling.

**Chromates.** *Hydrogen sulphide*, in acid solution, reduction to chromic salt with change of colour to green. *Lead acetate*, bright yellow precipitate ( $\text{PbCrO}_4$ ), insoluble in acetic acid.

*Silver nitrate*, dark red precipitate ( $\text{Ag}_2\text{CrO}_4$ ), soluble in hot concentrated nitric acid.

#### Iron.

*On charcoal*, grey magnetic metal. *Borax bead*, O.F. dark yellow, hot; pale yellow, cold; I.F. green.

**Ferrous salts.** *Ammonium sulphide*, black precipitate ( $\text{FeS}$ ), soluble in acids. *Potash*, *soda*, or *ammonia*, white precipitate, rapidly becoming green and then brown. *Potassium ferrocyanide*, white precipitate, gradually becoming dark blue. *Potassium ferricyanide*, dark blue precipitate  $\text{Fe}_3(\text{FeCy})_2$ . *Potassium thiocyanate*, no reaction.

**Ferric salts.** *Ammonium sulphide*, black precipitate ( $2\text{FeS} + \text{S}$ ), soluble in acids. *Potash*, *soda*, or *ammonia*, reddish brown precipitate ( $\text{Fe}_2\text{H}_2\text{O}_6$ ), soluble in acids. *Potassium ferrocyanide*, dark blue precipitate  $\text{Fe}_3(\text{FeCy})_2$ , insoluble in dilute acids. *Potassium ferricyanide*, no precipitate; greenish brown colouration. *Potassium thiocyanate*, blood-red colouration; not affected by boiling nor by hydrochloric acid.

#### Cerium.

*Borax* or *microcosmic salt*, O.F. orange red, hot; nearly colourless, cold; I.F. colourless.

*Ammonia*, white precipitate of basic salt; insoluble in excess. *Potash* or *soda*, white precipitate ( $\text{Ce}_2\text{H}_2\text{O}_6$ ); insoluble in excess; becomes yellow when exposed to air. *Oxalic acid*, white precipitate ( $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ ); insoluble in excess, but soluble in a large quantity of hydrochloric acid. *Potassium sulphate*, white precipitate even in somewhat acid solutions ( $\text{CeK}_3(\text{SO}_4)_3$ ); insoluble in saturated solution of potassium sulphate.

#### Beryllium.

*Ammonia*, white precipitate ( $\text{BeH}_2\text{O}_2$ ); insoluble in excess. *Potash* or *soda*, the same precipitate; soluble in excess, but reprecipitated on boiling (difference from Al). *Ammonium carbonate*, white precipitate; easily soluble in excess (difference from Al).

#### Uranium.

*Borax bead*, O.F. yellow, hot; pale yellow, cold; I.F. green. *Microcosmic salt*, O.F. yellow, hot; yellowish green, cold; I.F. green.

*Ammonia*, *potash*, or *soda*, yellow precipitate; insoluble in excess, but readily soluble in ammonium carbonate. *Ammonium sulphide*, brown precipitate; readily soluble in ammonium carbonate. *Potassium ferrocyanide*, chocolate brown precipitate; readily soluble in alkalis.

#### Titanium.

*Microcosmic salt*, O.F. colourless; I.F. yellow, hot; violet, cold, especially after adding a little tin. If ferrous sulphate is added the bead becomes blood red.

*Ammonia*, *potash*, *soda*, or *ammonium sulphide*, white precipitate  $\text{H}_2\text{TiO}_3$ ; insoluble in excess, soluble in dilute sulphuric and hydrochloric acids. *Potassium ferrocyanide*, dark brown precipitate. *Sodium thiosulphate*, complete precipitation on boiling.

#### Zinc.

*On charcoal*, incrustation of oxide; yellow, hot; white, cold. *With cobalt nitrate*, green mass.

*Ammonium sulphide*, white precipitate ( $\text{ZnS}$ ), soluble in dilute hydrochloric acid; insoluble in acetic acid and in alkalis. *Potash* or *soda*,

white precipitate ( $\text{ZnH}_2\text{O}_2$ ); soluble in excess. *Potassium ferrocyanide*, white precipitate insoluble in dilute hydrochloric acid ( $\text{Zn}_2\text{FeCy}_6$ ).

#### Manganese.

*Borax bead*, or *microcosmic salt*; O.F., violet; I.F., colourless. Fused with *potassium nitrate* and *sodium carbonate*, bluish-green mass ( $\text{K}_2\text{MnO}_4$ ).

*Ammonium sulphide*, pink precipitate ( $\text{MnS}$ ); soluble in dilute hydrochloric acid and in acetic acid. *Potash* or *soda*, white precipitate ( $\text{MnH}_2\text{O}_2$ ); insoluble in excess, becoming brown on exposure to air. Boiled with dilute *nitric acid* and *lead peroxide* (in absence of chlorine), a purplish crimson solution of permanganic acid.

#### Nickel.

*On charcoal*, grey magnetic metal. *Borax bead*, O.F., reddish brown; I.F., grey or colourless.

*Ammonium sulphide*, black precipitate ( $\text{NiS}$ ); somewhat soluble in excess; insoluble in cold dilute hydrochloric acid; soluble in strong acids. *Potash* or *soda*, pale green precipitate ( $\text{NiH}_2\text{O}_2$ ); insoluble in excess. *Potassium cyanide*, precipitate ( $\text{NiCy}_2$ ) soluble in excess, forming  $\text{NiCy}_2 \cdot 2\text{KCy}$ , which is not altered when boiled with exposure to air. This solution, heated with excess of sodium hypochlorite solution, or mixed with bromine in the cold, yields a precipitate of black nickelic hydroxide.

#### Cobalt.

*On charcoal*, grey magnetic metal. *Borax* or *microcosmic salt*, O.F. or I.F., dark-blue bead.

*Ammonium sulphide*, black precipitate ( $\text{CoS}$ ); insoluble in cold dilute hydrochloric acid; soluble in strong acids. *Potash*, pale-blue precipitate ( $\text{CoH}_2\text{O}_2$ ); slightly soluble in excess, forming a blue solution. *Potassium cyanide*, precipitate ( $\text{CoCy}_2$ ); soluble in excess, forming  $\text{CoCy}_2 \cdot 2\text{KCy}$ , and when this solution is boiled with exposure to air it is changed to  $\text{K}_3\text{CoCy}_6$ , which is not precipitated by sodium hypochlorite nor by bromine.

#### Vanadium.

*Borax bead*, O.F. yellow, hot; greenish yellow, cold; I.F. brownish, hot; emerald green, cold.

*Ammonium sulphide*, dark-brown solution, which when acidified yields a brown precipitate ( $\text{V}_2\text{S}_5$ ). *Ammonium chloride*, white precipitate of ammonium meta-vanadate ( $\text{NH}_4\text{VO}_3$ ). *Potassium ferrocyanide*, in acid solution, a green precipitate. If a solution of an alkaline vanadate is agitated with *hydrogen peroxide* and *ether*, the solution acquires a deep purplish red colour, but the ether remains colourless.

#### Calcium.

*Flame*, orange red.

*Ammonium carbonate*, white precipitate ( $\text{CaCO}_3$ ); soluble in acids. *Sulphuric acid*, white precipitate only in very concentrated solutions. *Ammonium oxalate*, white precipitate ( $\text{CaC}_2\text{O}_4$ ); insoluble in acetic and oxalic acids, but soluble in hydrochloric acid.

#### Strontium.

*Flame*, crimson.

*Ammonium carbonate*, white precipitate soluble in acids ( $\text{SrCO}_3$ ); *Ammonium sulphate*, white precipitate, especially on boiling. *Ammonium oxalate*, white precipitate ( $\text{SrC}_2\text{O}_4$ ); soluble in hydrochloric acid; insoluble in acetic acid. *Sulphuric acid* or *calcium sulphate*, white precipitate ( $\text{SrSO}_4$ ), forming slowly.

#### Barium.

*Flame*, apple green.

*Ammonium carbonate*, white precipitate ( $\text{BaCO}_3$ ); soluble in acids. *Ammonium oxalate*, white precipitate ( $\text{BaC}_2\text{O}_4$ ); soluble in hydrochloric acid; insoluble in acetic acid. *Sulphuric acid* or *calcium sulphate*, an immediate white precipitate, insoluble in acids and alkalis. *Potassium chromate*, yellow precipitate ( $\text{BaCrO}_4$ ); insoluble in acetic acid.

#### Magnesium.

*With cobalt nitrate*, a pink mass. No precipitate with group reagents. *Sodium phosphate*, in presence of ammonia and ammonium chloride, white precipitate rapidly becoming crystalline ( $\text{NH}_4\text{MgPO}_4$ ). Forms slowly in dilute solutions, formation being accelerated by agitation and by rubbing the sides of the beaker with a glass rod; soluble in acids.

#### Potassium.

*Flame colouration*, lavender.

*Platinum tetrachloride*, yellow crystalline precipitate  $\text{K}_2\text{PtCl}_6$ ; somewhat soluble in water, insoluble in alcohol. *Sodium hydrogen tartrate*, in neutral or feebly acid solutions, a white crystalline precipitate  $\text{KHC}_4\text{H}_4\text{O}_6$ , forming slowly in dilute solutions. If the solution contains free mineral acids, nearly neutralise with soda and add sodium acetate.

#### Ammonium.

Ammonium salts are readily volatile. *Heated with lime, potash, or soda*, ammonia gas is given off, and is recognised by its smell and its action on test paper.

*Platinum tetrachloride*, yellow crystalline precipitate ( $\text{NH}_4$ ) $_2\text{PtCl}_6$ ; slightly soluble in water, insoluble in alcohol. *Sodium hydrogen tartrate*, white crystalline precipitate ( $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$ ), forming slowly in dilute solutions.

#### Sodium.

*Flame colouration*, intense yellow.

Almost all sodium salts are soluble; sodium chloride, obtained by slow evaporation of a solution acidified with hydrochloric acid, crystallises in distinct cubes.

*Potassium metantimoniate*, white crystalline precipitate ( $\text{NaSbO}_3$ ); from neutral or slightly alkaline solutions.

#### Lithium.

*Flame colouration*, crimson.

*Platinum tetrachloride*, no precipitate. *Sodium phosphate*, white precipitate ( $\text{Li}_3\text{PO}_4$ ); soluble in hydrochloric acid, not reprecipitated by ammonia except on boiling. *Ammonium hydrogen fluoride*, a white precipitate ( $\text{LiF}$ ).

#### Cesium.

*Flame colouration*, violet.

*Platinum tetrachloride*, yellow crystalline precipitate  $\text{Cs}_2\text{PtCl}_6$ ; insoluble in boiling water. *Tartaric acid*, crystalline precipitate; somewhat soluble in water.

#### Rubidium.

*Flame colouration*, violet.

*Platinum tetrachloride*, yellow crystalline precipitate ( $\text{Rb}_2\text{PtCl}_6$ ); insoluble in boiling water. *Tartaric acid*, white crystalline precipitate; less soluble than the cesium compound.

#### ACTO RADICLES.

The acid radicles are arranged partly in the order of the systematic separation and partly

with a view to bring together those acids which are commonly associated or which resemble one another in their reactions. In all cases, unless otherwise specified, it is important that the solution should be neutral.

#### Sulphates.

*Barium chloride*, white precipitate ( $\text{BaSO}_4$ ); insoluble in acids and alkalis.

Sulphates heated on charcoal, with sodium carbonate (not in a coal-gas flame) are reduced to sulphides; and if the mass is placed on a silver coin, and moistened with water, the silver is blackened.

#### Sulphites.

*Hydrochloric acid*, sulphur dioxide evolved, but no sulphur precipitated. *Barium chloride*, white precipitate ( $\text{BaSO}_3$ ); soluble in hydrochloric acid. *Iodine solution*, sulphites are converted into sulphates. Neutralise, then *slightly acidify* with acetic acid; add excess of *zinc sulphate*, a small quantity of *sodium nitroprusside*, and *potassium ferrocyanide*. The precipitate of zinc ferrocyanide has a pink colour.

#### Thiosulphates.

*Hydrochloric acid*, sulphur dioxide evolved and sulphur precipitated. *Silver nitrate*, white precipitate ( $\text{Ag}_2\text{S}_2\text{O}_3$ ), rapidly changing to black ( $\text{Ag}_2\text{S}$ ); soluble in excess of alkaline thiosulphate, forming a much more stable solution. With *sodium nitroprusside*, *zinc sulphate*, and *potassium ferrocyanide*, the precipitate is white. *Iodine solution* converts soluble thiosulphates into tetrathionates, which give no precipitate with barium chloride.

**Thionic Acids** (v. C. J. Trans. 1880, 608).

#### Sulphides.

*Hydrochloric acid*, in most cases evolution of hydrogen sulphide, especially on heating. *Lead nitrate* or *acetate*, black precipitate ( $\text{PbS}$ ). *Silver nitrate*, black precipitate ( $\text{Ag}_2\text{S}$ ); insoluble in ammonia, sodium thiosulphate, and potassium cyanide. *Sodium nitroprusside*, in alkaline solutions an intense but somewhat fugitive violet colouration.

#### Phosphates.

*Barium chloride*, white precipitate  $\text{Ba}_3(\text{PO}_4)_2$ ; soluble in dilute acids. *Calcium chloride*, white precipitate  $\text{Ca}_3(\text{PO}_4)_2$ ; soluble in acetic acid. *Silver nitrate*, yellow precipitate  $\text{Ag}_3\text{PO}_4$ ; soluble in nitric acid and in ammonia. *Magnesium sulphate*, in presence of ammonium chloride and ammonia, white crystalline precipitate  $\text{NH}_4\text{MgPO}_4$ ; soluble in acids. *Ammonium molybdate*, in nitric acid solution, a yellow precipitate on heating; soluble in ammonia, and soluble in excess of an alkaline phosphate.

#### Phosphites.

*Barium chloride*, white precipitate ( $\text{BaHPO}_3$ ); soluble in hydrochloric acid. *Silver nitrate*, precipitate of metallic silver, especially in presence of ammonia, and on heating. *Mercuric chloride*, white precipitate ( $\text{Hg}_2\text{Cl}_2$ ), becoming grey ( $\text{Hg}$ ). Heated with *nitric acid*, phosphites are converted into phosphates.

#### Carbonates.

*Hydrochloric acid*, effervescence, with evolution of carbonic anhydride, which turns lime-water turbid. *Barium chloride*, white precipitate ( $\text{BaCO}_3$ ); soluble in acids with effervescence.

#### Borates.

*Barium chloride*, white precipitate in not too dilute solutions; soluble in acids.

Mix the solid substance with concentrated sulphuric acid in a small crucible, add alcohol and ignite; the alcohol flame is green, especially at the edges. Mix the solid substance with three parts potassium hydrogen sulphate and one part powdered fluorspar, and heat on platinum wire in the cold area of the flame; a bright green colouration (due to  $\text{BF}_3$ ) is observed.

#### Silicates.

Silicic acid, or silica heated on a bead of microcosmic salt, is not dissolved, but after cooling can be seen under a lens in the form of a skeleton.

Solutions of silicates heated with acids, ammonium chloride, or ammonium carbonate, deposit silicic acid. Dilute solutions must be evaporated to dryness, and on treating the residue with dilute hydrochloric acid insoluble silica is left.

Most silicates are insoluble in water; some are decomposed by acids; others are only decomposed by fusion with about four times their weight of a mixture of equal parts of sodium and potassium carbonates.

#### Oxalates.

*Barium chloride* or *calcium chloride*, white precipitate; insoluble in acetic acid, but soluble in hydrochloric acid.

Acidify with sulphuric acid, and add potassium permanganate; the colour of the latter is rapidly and completely discharged.

Heat the solid substance with concentrated sulphuric acid; carbonic anhydride and carbonic oxide are evolved. The latter burns with a blue flame.

#### Fluorides.

*Barium chloride*, white precipitate ( $\text{BaF}_2$ ) soluble in hydrochloric acid. *Silver nitrate*, no precipitate with soluble fluorides. *Concentrated sulphuric acid*, especially when heated, produces hydrogen fluoride, which attacks glass. The substance and acid are placed in a small leaden or platinum crucible, which is covered with a watch-glass protected by a thin coating of wax, part of which has been scratched away so as to expose the glass.

#### Chlorides.

*Silver nitrate*, a white precipitate ( $\text{AgCl}$ ); insoluble in nitric acid, soluble in ammonia; darkens when exposed to light. *Manganese dioxide* and *sulphuric acid*, evolution of chlorine on heating. *Potassium dichromate* and *strong sulphuric acid*, evolution of chromyl dichloride on heating. This forms with ammonia a yellow solution of ammonium chromate.

#### Bromides.

*Silver nitrate*, yellowish white precipitate ( $\text{AgBr}$ ); insoluble in nitric acid; moderately soluble in ammonia; readily soluble in potassium cyanide or sodium thiosulphate. *Manganese dioxide* and *sulphuric acid*, orange vapours of bromine, which turn starch paste orange. *Chlorine water* liberates bromine, which dissolves in ether or carbon bisulphide, forming an orange brown solution. Bromides heated with *potassium dichromate* and *strong sulphuric acid* yield bromine, which forms a colourless solution with ammonia.



**Iodides.**

*Silver nitrate*, yellow precipitate ( $\text{AgI}$ ); insoluble in nitric acid or ammonia; soluble in potassium cyanide or sodium thio-sulphate. *Manganese dioxide and sulphuric acid* yield violet vapours of iodine, which colour starch paste blue. *Chlorine water, bromine water, or potassium dichromate in presence of hydrochloric acid*, liberates iodine, which turns starch paste an intense blue. The colour disappears on heating, and reappears on cooling. The liberated iodine may be agitated with carbon bisulphide or chloroform, when it yields a violet solution. *Nitrogen oxides in sulphuric acid* likewise liberate iodine; but do not liberate bromine unless added in large excess.

**Cyanides.**

*Silver nitrate*, white precipitate ( $\text{AgCN}$ ); insoluble in nitric acid, but soluble in ammonia, sodium thiosulphate, or excess of the alkaline cyanide.

Add ferric chloride and ferrous sulphate; make alkaline with potash or soda, and then acidify with hydrochloric acid. A dark-blue precipitate of Prussian blue is formed.

Evaporate the solution with an excess of yellow ammonium sulphide to complete dryness on a water-bath; dissolve in very dilute hydrochloric acid, and add ferric chloride; a blood-red colouration is produced.

Most cyanides evolve hydrocyanic acid, recognisable by the smell, when treated with hydrochloric or sulphuric acid.

Mercuric cyanide cannot be recognised by these tests. It yields cyanogen when heated in a closed tube, and is decomposed when heated with strong sulphuric acid.

**Ferrocyanides.**

*Silver nitrate*, white precipitate ( $\text{Ag}_2\text{FeCy}_6$ ), insoluble in nitric acid and in ammonia; soluble in potassium cyanide. *Ferric chloride*, dark-blue precipitate ( $\text{Fe}_4(\text{FeCy}_6)_3$ ). *Ferrous sulphate*, white precipitate rapidly becoming blue. *Copper sulphate*, chocolate-brown precipitate ( $\text{Cu}_2\text{FeCy}_6$ ) or in very dilute solution a brown colouration.

**Ferrieyanides.**

*Silver nitrate*, orange precipitate ( $\text{Ag}_2\text{FeCy}_6$ ) soluble in ammonia, insoluble in nitric acid. *Ferrous sulphate*, dark-blue precipitate ( $\text{Fe}_3(\text{FeCy}_6)_2$ ) insoluble in dilute acids, decomposed by alkalis. *Ferric chloride*, a greenish-brown colouration.

**Thiocyanates.**

*Silver nitrate*, white precipitate ( $\text{AgCNS}$ ), soluble in ammonia, insoluble in nitric acid. *Ferric chloride*, blood-red colouration, not affected by boiling nor by hydrochloric acid; decolourised by mercuric chloride. *Copper sulphate*, a black precipitate changing to white ( $\text{Cu}_2(\text{CNS})_2$ ) on standing or addition of a reducing agent.

**Nitrates.**

Sulphuric acid evolves nitric acid on heating; if metallic copper is added, red-brown nitrogen oxides are given off.

The neutral solution is mixed with ferrous sulphate, and concentrated sulphuric acid is poured down the side of the tube so as to form a layer at the bottom; a dark-brown ring is formed at the junction of the two liquids. Iodine and bromine must be removed before applying this test, and the liquid must be cold.

**Nitrites.**

*Silver nitrate*, a white precipitate in concentrated solutions.

Mix the solution with potassium iodide and starch and acidify with acetic acid; a deep-blue colouration is produced owing to the liberation of iodine.

Nitrites heated with dilute acids evolve nitrogen oxides.

**Chlorates.**

Heat a small quantity of the solid with concentrated sulphuric acid, a yellow explosive gas is produced.

Acidify the solution with sulphuric acid, add indigo solution, and then sulphurous acid or a sulphite drop by drop. The colour of the indigo is discharged.

**Hypochlorites.**

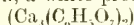
*Silver nitrate*, a white precipitate of silver chloride. *Lead nitrate*, a white precipitate becoming orange red, finally brown. *Manganous salts*, a brown precipitate ( $\text{MnO}_2 \cdot x\text{H}_2\text{O}$ ). *Indigo solution*, decolourised even in an alkaline solution.

**Tartrates.**

*Calcium chloride* in excess, a white precipitate ( $\text{CaC}_2\text{H}_3\text{O}_6$ ), soluble in acids and in potash solution. Complete precipitation requires time, and is promoted by vigorous agitation. *Potassium acetate*, in presence of free acetic acid, a white crystalline precipitate ( $\text{KHC}_2\text{H}_3\text{O}_6$ ) forming slowly in dilute solutions. *Silver nitrate*, a white precipitate soluble in nitric acid or ammonia. If the washed precipitate is dissolved in the least possible quantity of dilute ammonia, and the solution heated, the test tube is coated with a mirror of metallic silver.

**Citrates.**

*Calcium chloride*, or *lime water*, in excess in a neutral solution, a white precipitate



only on boiling. *Potassium salts*, no precipitate.

**Malates.**

*Calcium chloride*, no precipitate even on boiling, except in strong solutions; precipitate in dilute solutions on adding alcohol. *Lime water*, no precipitate even on boiling. *Silver nitrate*, white precipitate ( $\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6$ ), which becomes grey on boiling. *Lead acetate*, white precipitate ( $\text{PbC}_4\text{H}_4\text{O}_6$ ), which when washed melts in boiling water.

**Succinates.**

*Barium chloride*, or *calcium chloride*, no precipitate except after addition of alcohol. *Ferric chloride*, reddish-brown precipitate ( $\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_6)_3$ ), soluble in acids; decomposed by ammonia.

**Benzoates.**

*Hydrochloric acid*, white crystalline precipitate of benzoic acid, slightly soluble in water. *Ferric chloride*, a buff precipitate ( $\text{Fe}_2(\text{C}_7\text{H}_5\text{O}_2)_3$ ) soluble in hydrochloric acid with liberation of benzoic acid; decomposed by ammonia.

**Salicylates.**

*Ferric chloride*, intense purple colour; not affected by glycerol; interfered with by alkalis, dilute mineral acids, tartaric, citric, and oxalic acids, and certain other substances such as borax, sodium phosphate, ammonium and sodium acetates. *Silver nitrate*, white precipitate in

neutral solutions. *Bromine water*, white precipitate which with sodium amalgam yields phenol.

#### Acetates.

*Ferric chloride*, a dark-red colouration, discharged on boiling, with precipitation of a basic ferric acetate. Also discharged by hydrochloric acid. Heated with *strong sulphuric acid*, acetic acid is evolved. If alcohol is added, ethyl acetate is formed and is recognised by the smell.

#### Formates.

*Silver nitrate*, a white precipitate in concentrated solutions; the solution or precipitate rapidly becomes black (Ag), especially on heating. *Ferric chloride*, a red colour, discharged on boiling, with precipitation of basic ferric formate; also discharged by hydrochloric acid.

A solid formate heated with concentrated sulphuric acid gives off carbonic oxide, but no carbonic anhydride.

#### Gallic acid.

*Ferric chloride* in neutral solutions, a bluish-black precipitate or colouration. *Gelatin* or *albumen*, no precipitate. *Potassium cyanide*, red colouration, which disappears on standing but reappears on agitation in presence of air.

#### Tannic acid.

*Ferric chloride*, bluish-green or bluish-black precipitate or colouration. *Gelatin* or *albumen*, yellowish-white precipitate. *Potassium cyanide*, no colouration.

### QUANTITATIVE ANALYSIS.

A few metals are separated and weighed in the metallic condition, but the majority of elements and acid radicles are weighed in the form of one or other of their compounds. In order that a compound may be available for the determination of one of its constituents, it must be of perfectly definite composition and not highly hygroscopic or otherwise liable to alter; it must be insoluble in the liquid in which it is formed and insoluble in an excess of the reagent; it must be easily freed from impurities and capable of being brought into the proper condition for weighing without tedious and complicated operations. It is also desirable that the compound should contain only a small proportion of the constituent to be estimated, since the effect of the unavoidable error of experiment is thus minimised. An estimation of chlorine in the form of silver chloride is more accurate than an estimation of silver in the same way, since only one-fourth of the error of experiment represents chlorine, whilst three-fourths represents silver.

The forms in which metals are estimated are somewhat limited. A description will first be given of methods which are applicable to several metals, then an alphabetical list of metals and acid radicles with a summary of methods available in each case, followed by a series of methods of separation of general applicability. Special methods for the analysis of technical products will be found under special articles.

### GENERAL METHODS OF ESTIMATION.

#### I. As Sulphides.

(a) *With previous precipitation by hydrogen sulphide*. The solution should be moderately dilute and distinctly acidified with HCl, but any

large quantity of this acid must be avoided. Nitric acid and nitrates should be absent as far as possible; if present a much higher degree of dilution is necessary. In most cases precipitation is accelerated and the precipitate rendered more granular by keeping the liquid warm. A current of washed hydrogen sulphide is passed through the solution until it is thoroughly saturated, and the flask is closed and allowed to stand in a warm place until the precipitate has settled. Molybdenum and the metals of the platinum group are only completely precipitated after prolonged treatment with the gas. The precipitate is protected from air as far as possible during filtration, and the liquid used for washing should contain hydrogen sulphide in order to prevent oxidation.

When arsenic is present the liquid should be heated with pure sulphurous acid to reduce arsenic acid, and the excess of sulphurous acid expelled before treatment with hydrogen sulphide. In presence of antimony, tartaric acid should be added to prevent co-precipitation of basic antimony chloride.

When copper is precipitated as sulphide in presence of zinc, the copper sulphide should be washed once or twice with dilute hydrochloric acid of sp.gr. 1.05 containing hydrogen sulphide, and then with water also containing the gas.

Nitric acid may be removed by evaporating two or three times with concentrated hydrochloric acid, but this treatment is not admissible if the metal present forms a volatile chloride.

(β) *With previous precipitation by ammonium sulphide*. Add to the warm solution a considerable quantity of ammonium chloride, which is found to promote precipitation and render the precipitate more granular, then ammonia to alkaline reaction, and a slight excess of ammonium sulphide. Close the flask and allow to stand in a warm place until the precipitate has settled. Protect from air as far as possible during filtration and wash with water containing ammonium chloride and a little ammonium sulphide or hydrogen sulphide.

The precipitated sulphide is treated in one of two ways. It is collected on a weighed filter, dried at a definite temperature and weighed; or it is heated with sulphur in a current of hydrogen and then weighed.

In the first case it is essential to ensure the absence of co-precipitated sulphur, and for this purpose the dried precipitate is treated with pure carbon bisulphide and again dried, or in the case of cadmium, mercury, or bismuth the moist precipitate is treated with a warm concentrated solution of sodium sulphite, again washed, and dried.

When the sulphide is stable at a moderately high temperature and is not reduced by hydrogen, Rose's method is employed. The dry precipitate is separated from the filter, which is then burnt, and the precipitate and filter ash are introduced into a porcelain crucible and mixed with pure finely powdered sulphur. The crucible is provided with a perforated lid, through which passes a porcelain tube connected with a hydrogen apparatus. A current of purified and dried hydrogen is passed into the crucible, which is gradually heated to full redness until excess of

sulphur is expelled, allowed to cool in a current of hydrogen, and weighed.

#### II. As Oxide.

(a) *With previous precipitation as hydroxide.* The solution is mixed with ammonium chloride, heated to boiling, and ammonia added in slight excess. A large excess of ammonia will partially redissolve some of the precipitate and must be expelled by boiling. The precipitate is washed with hot water.

If ammonia is inadmissible, pure potash or soda is used as the precipitant. Excess of alkali must be avoided, and the precipitate must be very thoroughly washed, since small quantities of alkali are somewhat firmly retained.

In both cases it is better to precipitate in a porcelain or platinum vessel than in glass.

Non-volatile carbon compounds, such as sugar, glycerol, alkaline tartrates and citrates, &c., more or less completely prevent precipitation of hydroxides by potash, soda, or ammonia, and hence must first be removed by calcination.

#### (b) *With previous precipitation as carbonate.*

The solution is nearly neutralised, heated to boiling, and mixed with a slight excess of sodium carbonate, boiling being continued until all carbon dioxide is expelled. The precipitate is washed with hot water. Ammonium carbonate can be used in some cases and has the advantage of not introducing a fixed alkali. In these cases the precipitate should be washed with water containing a little ammonia and ammonium carbonate.

The precipitated hydroxide or carbonate is placed in a crucible (with previous separation from the filter paper if the metal is easily reducible) and is gradually heated to full redness, care being taken that no reducing gases from the flame enter the crucible. Oxides of reducible metals must be heated in a porcelain crucible, but in other cases a platinum crucible may be used with advantage. If carbonates (or oxalates) are being converted into oxides, it is important to secure a circulation of air in order to remove carbon monoxide and carbon dioxide as fast as they are given off, and thus accelerate decomposition. This is done by inclining the crucible and placing the lid across the mouth in a slanting position.

#### III. As reduced Metals.

(a) In some cases the metal is precipitated as oxide, which is then dried and heated in hydrogen as in Rose's method for sulphides, the reduced metal being cooled in hydrogen and weighed. This method is especially valuable when, as in the case of cobalt, the oxide obstinately retains small quantities of alkali, which however can readily be removed from the reduced metal by washing with water.

(b) The other method is to mix the oxide, carbonate, &c., with five or six times its weight of ordinary potassium cyanide, and heat in a capacious porcelain crucible, at first cautiously and afterwards to complete fusion. When reduction is complete the crucible is allowed to cool, and is tapped occasionally to promote the collection of the reduced metal in a single button. The cyanide is removed by treatment with water, the metal washed, dried, and weighed. Care should be taken that it is not mixed with small

fragments of porcelain resulting from the corrosion of the crucible.

#### IV. As Sulphate.

Barium, strontium, and lead are precipitated from solutions in the ordinary way, but other metals are converted into sulphate by treatment with the strong acid, the method being only available when a single metal is present in combination with a volatile acid. The highly concentrated solution, or better, the solid substance, is mixed cautiously with concentrated sulphuric acid in a platinum crucible and then gently heated to expel excess of acid, the crucible being inclined and the lid placed in a slanting position across its mouth. A large excess of acid should be avoided, and care must be taken that the temperature is sufficient to expel the excess of free acid but not sufficient to decompose the sulphate. Sulphates of the alkalis and alkaline earths may be heated to redness. Bismuth sulphate and zinc sulphate decompose if heated above  $400^{\circ}$ ; magnesium sulphate is not decomposed at  $450^{\circ}$ , nor barium or lead sulphate at  $500^{\circ}$  (G. H. Bailey). A temperature of about  $350^{\circ}$  is required to expel the last traces of free sulphuric acid. With lead or bismuth sulphate a porcelain vessel must be used.

#### DETERMINATION OF METALS AND ACID RADICLES.

Details of operations will be found under *General Methods of Estimation* (v. p. 122).

##### Aluminium.

(a) *As oxide*, with previous precipitation with ammonium sulphide, ammonium carbonate, or as basic acetate (v. *Methods of Separation*).

(b) *As phosphate*. The solution is nearly neutralised, mixed with sodium acetate and a small quantity of acetic acid, heated to boiling, sodium phosphate added in excess, and the precipitate washed with hot water, heated, and weighed as aluminium phosphate  $\text{AlPO}_4$ .

##### Ammonium.

(a) *As platinumchloride*  $(\text{NH}_4)_2\text{PtCl}_6$  (v. *Potassium*). The platinum chloride solution should be added before the liquid is heated, and evaporation should not quite be carried to complete dryness.

(b) *By distillation* (v. *ACIDIMETRY*).

##### Antimony.

(a) *As sulphide*,  $\text{Sb}_2\text{S}_3$  (v. I.). The precipitate is collected on a weighed filter, dried at  $100^{\circ}$ , and weighed. An aliquot part is then placed in a porcelain boat, and heated in a glass tube in a current of dry carbonic anhydride until it becomes black and all admixed sulphur is expelled. The loss of weight is calculated to the whole quantity and deducted from the weight at  $100^{\circ}$ .

(b) *As oxide*,  $\text{Sb}_2\text{O}_3$ , with previous precipitation as sulphide. The sulphide is placed in a porcelain crucible and treated with fuming nitric acid boiling at  $86^{\circ}$  until completely oxidised, the excess of acid expelled, and the residue heated with partial exposure to air until the weight is constant. The sulphide may also be mixed with 30 to 50 times its weight of precipitated mercuric oxide and heated cautiously until all vapours cease to come off.

##### Arsenic.

(a) *As sulphide*,  $\text{As}_2\text{S}_3$  (v. I.), which is dried at  $100^{\circ}$ . The dry precipitate should volatilise completely when heated.



Arsenic acid is estimated as *magnesium pyro-arsenate*,  $\text{Mg}_2\text{As}_2\text{O}_7$ , in the same way as phosphoric acid (which see). The filter paper is moistened with a solution of ammonium nitrate and dried before burning, in order to prevent reduction (Reichel). It can also be estimated indirectly by means of standard iodine solution.

Arsenious acid, by standard iodine solution (*v. Volumetric Methods*).

#### **Barium.**

(a) As *sulphate*,  $\text{BaSO}_4$ , by precipitation with sulphuric acid (*v. Sulphuric acid*).

(b) As *carbonate*,  $\text{BaCO}_3$ , which may be dried at a temperature below dull redness after moistening the filter ash with ammonium carbonate (*v. Methods of Separation*, p. 128).

(c) As *silicofluoride* (*v. Methods of Separation*).

#### **Beryllium.**

(a) As *oxide*,  $\text{BeO}$ , with previous precipitation by ammonia or ammonium sulphide, but not soda, potash, or ammonium carbonate.

#### **Bismuth.**

(a) As *oxide*,  $\text{Bi}_2\text{O}_3$ , after precipitation with a slight excess of ammonium carbonate. In presence of chlorides or sulphates the precipitate will contain basic chloride or sulphate, and in this (or in any other) case the bismuth may be precipitated as sulphide, which is oxidised in the crucible by fuming nitric acid boiling at  $86^\circ$ , and then heated.

(b) As *sulphide*,  $\text{Bi}_2\text{S}_3$ , which is dried at  $100^\circ$  and weighed at intervals of 20–30 minutes. The weight first decreases owing to loss of water, and then increases owing to oxidation; the minimum weight is taken as correct.

(c) As *metallic bismuth* (*v. III*).

(d) *Volumetrically* by potassium bichromate.

#### **Cadmium.**

(a) As *sulphide*,  $\text{CdS}$ , which is dried at  $100^\circ$ .

(b) *Volumetrically* by potassium permanganate.

#### **Calcium.**

(a) As *oxide*,  $\text{CaO}$ , after precipitation with ammonium carbonate or ammonium oxalate. In the latter case the solution is made alkaline with ammonia, heated to boiling, and mixed with excess of ammonium oxalate. The precipitate is washed with hot water and strongly heated until its weight is constant.

**Chromium** as chromic salts.

(a) As *oxide*,  $\text{Cr}_2\text{O}_3$ , after precipitation by ammonia, or better, ammonium sulphide.

(b) As *phosphate* in the same way as aluminium.

**Chromium** as chromic acid.

(a) As *oxide*,  $\text{Cr}_2\text{O}_3$ . The solution is neutralised, heated to boiling, and mixed with excess of a neutral solution of mercurous nitrate free from nitrous acid. The precipitate is washed with hot water containing mercurous nitrate and heated to redness in a porcelain crucible until all mercurial vapours are expelled. The mercurous chromate yields chromic oxide.

(b) *Volumetrically*. The solution is acidified with sulphuric acid, mixed with a measured excess of a standard solution of ferrous sulphate, and the excess of iron determined by means of standard potassium bichromate  $\text{CrO}_3 = \text{Fe}_3$ .

When chromic salts and chromates occur together, the chromic acid is estimated volu-

metrically, and the total chromium is determined as oxide in another portion of the solution after reducing the chromic acid by treating with sulphurous acid or alcohol.

#### **Cobalt.**

(a) As *metallic cobalt*, after precipitation as hydroxide by soda or potash (*v. III. a*). The solution must be free from ammonium salts or all ammonia must be expelled by boiling. The precipitate retains traces of alkali, and in accurate estimations the reduced metal should be washed with water, dried, and again heated in hydrogen.

(b) As *sulphate*,  $\text{CoSO}_4$ , after precipitation as sulphide, which is treated with nitric acid and then with sulphuric acid (*v. IV*). If the heated sulphate is at all black it must be treated again with sulphuric acid.

#### **Copper.**

(a) As *cuprous sulphide*,  $\text{Cu}_2\text{S}$ , using Rose's method, with previous precipitation as cupric sulphide by hydrogen sulphide.

(b) As *oxide* after precipitation by potash or soda in absence of ammonium salts.

(c) As *cuprous thiocyanate*,  $\text{CuCNS}$ . The solution, which must contain no free nitric acid, is slightly acidified with hydrochloric acid, heated to boiling, and mixed gradually with an excess of a moderately strong solution of equal parts of ammonium or potassium thiocyanate and sodium hydrogen sulphite. When cold the precipitate is collected on a weighed filter, washed with cold water and dried at  $100^\circ$ . The precipitate may also be converted into cuprous sulphide by Rose's method. Cuprous thiocyanate is not quite insoluble, especially in presence of much free acid.

(d) *Volumetrically*, and

(e) *Electrolytically*.

#### **Gold.**

As *metallic gold*. Nitric acid is removed by evaporation with hydrochloric acid. The solution is acidified with hydrochloric acid, mixed with a large excess of ferrous sulphate solution, and heated gently for a few hours; or it is acidified with sulphuric acid, mixed with oxalic acid, and allowed to stand in a warm place for several hours. The precipitate is collected on a weighed filter, washed and dried.

#### **Iron.**

(a) As *ferric oxide*,  $\text{Fe}_2\text{O}_3$ , after precipitation by ammonia, potash, or soda, or as basic carbonate or basic acetate. The oxide is heated to redness until its weight is constant; if heated at a higher temperature it is partially converted into ferroso-ferric oxide,  $\text{Fe}_3\text{O}_4$ .

(b) As *sulphide*, by Rose's method, after precipitation by ammonium sulphide.

(c) *Volumetrically* by potassium permanganate or bichromate.

When ferrous and ferric salts exist in solution together, the total iron is determined in an aliquot portion by completely oxidising by nitric acid or bromine water and precipitating as ferric oxide, or by completely reducing and titrating with permanganate or bichromate. The ferrous iron is determined in another part by permanganate or bichromate. If the substance is solid it is dissolved in acid in an atmosphere of carbonic anhydride and the ferrous salt determined by titration. Silicates and similar substances are heated in sealed tubes at  $200^\circ$  with a mixture

of strong sulphuric acid (4 parts) and water (1 part), and the solution titrated with permanganate.

#### Lead.

(a) As *sulphate*,  $\text{PbSO}_4$ . The solution, which should not be dilute, is mixed with dilute sulphuric acid and twice its volume of alcohol, and allowed to stand, and the precipitate is washed with alcohol. If the addition of alcohol is inadmissible the solution is evaporated to small bulk, mixed with a large excess of dilute sulphuric acid, and allowed to stand. The precipitate is washed with dilute sulphuric acid and afterwards with alcohol to remove all free acid.

(b) As *sulphide*,  $\text{PbS}$ , by hydrogen sulphide and Rose's method.

(c) As *oxide*,  $\text{PbO}$ , after precipitation by ammonium carbonate, avoiding the presence of an excess of ammonium salts.

(d) As *metal*.

(e) *Volumetrically* by permanganate.

#### Magnesium.

(a) As *pyrophosphate*,  $\text{Mg}_2\text{P}_2\text{O}_7$ . The solution is mixed with ammonium chloride in sufficient quantity to prevent precipitation by ammonia, made strongly alkaline with ammonia, and then mixed with excess of sodium phosphate, or, better, ammonium phosphate or microcosmic salt. Care should be taken to avoid rubbing or scratching the sides of the vessel. The liquid is allowed to stand for a few hours, filtered, and the precipitate washed with a mixture of strong ammonia (1 part) and water (5 parts) until the washings give only a faint opalescence with silver nitrate after acidifying with nitric acid. The precipitate is dried, *cautiously* heated in a platinum crucible until all ammonia is expelled, and then heated to redness until the weight is constant. If the precipitate is black, owing to partial reduction, it is moistened with a few drops of strong nitric acid and again heated until perfectly white.

#### Manganese.

(a) As *sulphide*,  $\text{MnS}$ , by Rose's method after precipitation by ammonium sulphide.

(b) As *oxide*,  $\text{Mn}_2\text{O}_3$ , after precipitation by soda or potash or by sodium carbonate, ammonium salts being absent.

(c) As *pyrophosphate*,  $\text{Mn}_2\text{P}_2\text{O}_7$ , (*v. Magnesium*).

#### Mercury (as mercurous compounds).

(a) As *mercurous chloride*,  $\text{Hg}_2\text{Cl}_2$ . The dilute cold solution is mixed with a solution of sodium chloride in slight excess, and the precipitate is collected on a weighed filter and dried at  $100^\circ$ .

#### Mercury (as mercuric compounds).

(a) As *sulphide*,  $\text{HgS}$ , which is dried at  $100^\circ$  after precipitation by hydrogen sulphide.

(b) As *mercurous chloride*,  $\text{Hg}_2\text{Cl}_2$ . The solution is mixed with excess of hydrochloric acid and phosphorous acid (made by allowing phosphorus to oxidise slowly in moist air), and allowed to stand in a warm place for twelve hours. The precipitate is collected on a weighed filter and dried at  $100^\circ$ .

#### Molybdenum.

(a) As *lead molybdate*,  $\text{PbMoO}_4$ . The solution is heated to boiling, mixed with excess of lead acetate, and boiled for a few minutes. The precipitate is washed with hot water, dried at

$100^\circ$ , and heated to low redness in a porcelain crucible.

(b) As the *oxide*,  $\text{MoO}_3$ . The solution is neutralised with nitric acid, mixed with excess of a neutral solution of mercurous nitrate, the precipitate washed with mercurous nitrate solution, dried, and heated in Rose's apparatus in a current of hydrogen until the weight is constant.

#### Nickel.

(a) As *oxide*,  $\text{NiO}$ , after precipitation by potash or soda in absence of ammonium salts; or after precipitation by ammonium sulphide thoroughly saturated with hydrogen sulphide, the nickel sulphide being dissolved in aqua regia and the solution precipitated by soda or potash.

(b) *Electrolytically*.

#### Platinum.

(a) As *metal*. The solution of platinum chloride free from excess of acid is precipitated by ammonia, or, better, potassium chloride (*v. Potassium*), and the precipitate is filtered by Gooch's method or through a plug of thoroughly dried asbestos contained in a weighed tube. The precipitate is dried, heated to redness in a current of hydrogen, washed with water to remove alkaline chloride, again dried, and weighed.

#### Potassium.

(a) As *platinochloride*,  $\text{K}_2\text{PtCl}_6$ . The solution, which must contain the potassium in the form of chloride and be free from acid, is mixed with excess of platinum chloride and evaporated to dryness on the water-bath. The crystalline residue is washed with strong alcohol, without breaking the crystals, until the washings (which at first must be orange, showing the presence of excess of platinum) are colourless. The precipitate is left in the evaporating dish and the washings are poured through a small filter. When washing is complete the precipitate is transferred to a weighed porcelain crucible by means of a jet of alcohol from a wash-bottle, and the alcohol is decanted off through the filter. The precipitate in the crucible is dried first at  $70^\circ$  till most of the alcohol is expelled and then at  $100^\circ$  for half an hour. The filter is dried, and any precipitate is detached from the paper as far as possible and added to the contents of the crucible, which is then weighed. The filter is burnt, and the ash allowed to fall into the crucible, which is again weighed. The increase in weight is filter ash and metallic platinum. The amount of platinochloride corresponding with the latter is calculated and added to the weight of the precipitate.

#### Selenium.

As *selenium*. The solution is strongly acidified with hydrochloric acid, mixed with excess of sulphurous acid or sodium hydrogen sulphite, and boiled for about fifteen minutes. The precipitate is collected on a weighed filter and dried at a temperature below  $100^\circ$ . Solutions of selenium containing hydrochloric acid cannot safely be concentrated by evaporation except in presence of a large quantity of alkaline chlorides, which prevent the volatilisation of the selenium as chloride.

#### Silver.

(a) As *chloride*,  $\text{AgCl}$ , or *bromide*,  $\text{AgBr}$ . The solution is acidified with nitric acid, heated to boiling, and mixed with a slight excess of sodium chloride or potassium bromide. Estimation as

bromide is to be recommended, since silver chloride is not quite insoluble in pure water. The precipitate is washed with hot water, dried, detached from the paper as far as possible, transferred to a porcelain crucible, and dried at  $150^{\circ}$ , or heated slowly until it shows signs of fusion at the edges, and weighed. The filter is burnt and the ash added to the crucible, which is again weighed. The increase in weight is filter ash and metallic silver. The quantity of bromide or chloride corresponding with the latter is calculated and added to the weight of the precipitate.

(b) *Volumetrically (v. Silver).*

(c) *Electrolytically.*

**Sodium** is weighed in the form of chloride together with any potassium which may be present, and is estimated by difference, or it may be estimated directly as sulphate or chloride if potassium is absent.

#### **Strontium.**

(a) *As sulphate,  $\text{SrSO}_4$ .* The solution, which must contain but little free acid, is mixed with excess of dilute sulphuric acid and at least an equal volume of alcohol, and the precipitate is washed with alcohol. If alcohol cannot be used a much larger excess of sulphuric acid is added and the precipitate is washed with cold water, but the results are less exact.

(b) *As carbonate,  $\text{SrCO}_3$*  (which must not be heated too strongly) after precipitation by ammonium carbonate.

#### **Thallium.**

(a) *As thallous iodide  $\text{TlI}$ .* The solution is heated with sulphurous acid to reduce all the thallium compounds to thallous salts, allowed to cool, and then mixed with excess of potassium iodide. The precipitate is washed with dilute alcohol, and dried on a weighed filter at  $100^{\circ}$ .

#### **Tin.**

(a) *As oxide,  $\text{SnO}_2$ ,* which is obtained when tin or one of its alloys is treated with nitric acid. The solution is boiled for ten minutes to ensure complete precipitation, and the precipitate is digested for an hour with dilute nitric acid (1 : 6) at  $100^{\circ}$  to remove other metals, washed with hot water, and ignited.

In other cases the tin is precipitated as hydrated oxide. If the solution contains stannous salts the latter are oxidised by chlorine or by hydrochloric acid and potassium chlorate, ammonia added until a slight precipitate forms, and hydrochloric acid until the precipitate just redissolves. The solution is then mixed with a moderately large quantity of a strong solution of ammonium nitrate or sodium sulphate, and boiled for some time. The precipitate is washed with hot water by decantation and on the filter, dried, and heated. To ascertain if precipitation is complete, a small quantity of the filtrate is added to a hot solution of ammonium nitrate or sodium sulphate.

If the tin has been precipitated as stannic sulphide the latter is washed with a solution of sodium chloride, and finally with a solution of ammonium acetate, dried, and roasted in a porcelain crucible until the weight is constant. Decomposition is facilitated by adding a small quantity of ammonium carbonate.

In all cases the filter is burnt separately and the ash dropped into the crucible.

#### **Titanium.**

(a) *As dioxide,  $\text{TiO}_2$ ,* after precipitation by ammonia. Usually the substance is dissolved in sulphuric acid, or is fused with potassium hydrogen sulphate and dissolved in water. The solution is diluted largely and boiled for some time, when all titanium is precipitated as hydrated oxide, which is rendered anhydrous by ignition. The solution should contain 0.5 p.c. of free sulphuric acid; if less, the precipitate is impure, if more, precipitation is incomplete (Lévy). In presence of iron the results are always somewhat too high.

#### **Tungsten.**

*As tungstic anhydride  $\text{WO}_3$ .* The solution containing the tungsten as an alkaline tungstate is neutralised with nitric acid and precipitated with a neutral solution of mercurous nitrate. The precipitate is washed with a solution of mercurous nitrate, dried, and heated in a porcelain crucible, when tungstic anhydride is left.

#### **Uranium.**

*As the oxide,  $\text{U}_3\text{O}_8$ .* The solution, oxidised if necessary by nitric acid, is heated to boiling and mixed with a slight excess of ammonia. The precipitate of acid ammonium uranate is washed with ammonium chloride solution, dried, and strongly heated.

#### **Vanadium.**

(a) *As barium vanadate,  $2\text{BaO.V}_2\text{O}_5$ .* The solution is neutralised with ammonia, heated to boiling, mixed with excess of barium chloride, agitated, and cooled quickly out of contact with air. The precipitate is washed and heated.

(b) *As manganese vanadate,  $2\text{MnO.V}_2\text{O}_5$ .* The solution is mixed with a slight excess of ammonium chloride and ammonia, manganese chloride or sulphate mixed with ammonium chloride is added in excess, and the liquid is boiled two or three minutes and allowed to cool out of contact with the air. The precipitate, which should be brownish yellow and free from oxidation products, is washed with cold water and heated.

For other methods of estimating and separating vanadium v. A. Carnot, C. R. 104, 1803 & 1850, C. J. Abstracts, 1837, 893.

#### **Zinc.**

(a) *As oxide,  $\text{ZnO}$ ,* with previous precipitation by sodium carbonate in absence of ammonium salts.

(b) *As sulphide,  $\text{ZnS}$ ,* by Rose's method after precipitating with ammonium sulphide.

#### **ACID RADICLES.**

##### **Carbonic acid v. ACIDIMETRY.**

When carbonates and sulphides occur together, the gases evolved on treatment with acid are passed into a solution of copper acetate acidified with acetic acid and heated to boiling. Hydrogen sulphide is absorbed, with formation of copper sulphide, and carbon dioxide passes on.

##### **Chloric acid.**

Any chlorine present as chloride is determined, the chlorate reduced by a zinc-copper couple, and the chlorine again determined. The difference is the amount of chlorine existing as chlorate (Thorpe, C. J. 1873, 541). Thin granulated zinc is washed with soda solution, then with dilute sulphuric acid, which is allowed to act for a short time, and finally with water. It is then covered with about 100 cc. of a 3 p.c.



solution of copper sulphate heated to  $40^{\circ}$ – $50^{\circ}$ . When most of the copper has been deposited the liquid is carefully poured off, and treatment repeated with a fresh quantity of solution. The zinc-copper couple is now very carefully washed with distilled water by decantation, not more than 0.5 gram potassium chlorate, or the equivalent quantity of any other chlorate, is weighed out into the beaker and dissolved in about 25 cc. of warm water, which should just cover the couple. The liquid is heated gently for half an hour, then boiled for half an hour, dilute sulphuric acid added drop by drop until the white precipitate of zinc hydroxide and oxychloride just dissolves, filtered, the filtrate neutralised with pure calcium carbonate, and the chlorine estimated by standard silver nitrate solution (C. J. Trans. 1888, 166).

#### Hydrobromic, hydrochloric, and hydriodic acids.

(a) As silver salts (AgBr, AgCl, AgI). The solution is mixed with excess of silver nitrate, acidified with nitric acid, and heated to boiling. The precipitate is treated exactly as in the estimation of silver.

(b) *Volumetrically* with silver nitrate.

#### Hydrofluoric acid.

(a) As *calcium fluoride*,  $\text{CaF}_2$ , in the case of soluble fluorides. The solution is mixed with a moderate excess of sodium carbonate, heated to boiling, and mixed with excess of calcium chloride. The precipitate is washed, dried, and heated to redness in a platinum crucible, then treated with excess of acetic acid, evaporated to dryness, and heated to expel excess of acid. The product is now heated with water, and the insoluble calcium fluoride filtered off, washed, and heated.

(b) Indirectly as *silicon fluoride*,  $\text{SiF}_4$ . The finely-powdered solid substance is placed in a deep platinum crucible and covered with three or four times its weight of pure precipitated silica, the weight of which is accurately known. Sulphuric acid is then added, and the crucible gently heated for half an hour. The temperature is raised to expel most of the sulphuric acid, the residue treated with hydrochloric acid, washed, dried, and heated. The hydrofluoric acid is calculated from the loss in weight of the silica  $4\text{HF} = \text{SiO}_2$ . The amount of silica in the substance must be known, and its weight added to that of the admixed silica.

#### Hydrosulphuric acid.

(a) Soluble sulphides are estimated volumetrically by iodine solution.

(b) Insoluble sulphides are decomposed by hydrochloric acid in a flask similar to that used in the gravimetric estimation of carbonic acid, and the gas evolved is led into two or three bulb U-tubes containing a solution of bromine in dilute hydrochloric acid, which converts the hydrogen sulphide into sulphuric acid. When decomposition is complete, the liquid in the flask is boiled, and the last traces of the gas are drawn through the bulbs by means of an aspirator. The contents of the bulb tubes are transferred to a beaker, heated to expel bromine, and the sulphuric acid precipitated by barium chloride.

Sulphides which are not decomposed by hydrochloric acid may be oxidised with aqua regia, hydrochloric acid and bromine, or hydrochloric

acid and potassium chlorate, the sulphuric acid formed being weighed as barium sulphate.

#### Nitric acid.

(a) Indirectly, as ammonia, by means of the zinc-copper couple (Thorpe). A zinc-copper couple (*v. Chloric acid*) is made in a flask into which is weighed a quantity of the nitrate corresponding with not more than 0.5 gram of potassium nitrate, and sufficient water is added to just cover the couple. The flask is attached to a condenser, the other end of which is connected with a U-tube or flask containing hydrochloric acid, as in the estimation of ammonia. The liquid is gently heated for some time, and then distilled nearly to dryness. After cooling, a further quantity of water is added to the couple, and distillation repeated. The ammonia in the distillate is estimated as platinumchloride, or is received in a measured volume of standard acid and titrated.

(b) *Schloesing's method*. When a solution of a nitrate is heated with an acid solution of a ferrous salt, the nitrate is decomposed, the whole of the nitrogen being evolved as nitric oxide, which is measured. The difficulty lies mainly in obtaining the nitric oxide free from air. The apparatus employed consists of a small distilling flask provided with a side tube which terminates under a gas-collecting tube in a mercurial trough. The neck of the flask is fitted with a cork, which carries a tube funnel provided with a stop-cock and another tube connected with a carbon dioxide apparatus. Carbon dioxide *free from air* is passed into the apparatus until all air is expelled and the gas issuing from the exit tube is completely absorbed by potash. The substance containing the nitrate, which must be in the solid condition, is dissolved in 2 or 3 c.c. of concentrated ferrous chloride solution, mixed with 1 c.c. of strong hydrochloric acid, and introduced into the flask by means of the funnel tube, care being taken that no air enters. The dish and the funnel are rinsed with very small quantities of acid, the object being to use as little liquid as possible. The contents of the flask are then rapidly boiled to dryness, the evolved gas being collected in the tube over mercury, and carbon dioxide is driven through the apparatus to expel all nitric oxide. The mixture of nitric oxide and carbon dioxide is transferred to an apparatus for gas analysis; the latter absorbed by potash, and the former mixed with oxygen and absorbed by alkaline pyrogallol. Nitrites are converted into nitrates by addition of hydrogen peroxide during evaporation of the original solution (*v. Warington*, C. J. Trans. 1880, 468, and 1882, 345).

(c) *By standard indigo solution* (Warington, C. N. 35, 45, and C. J. Trans. 1879, 578).

#### Oxalic acid.

(a) As *calcium oxalate*. The solution is neutralised with ammonia, heated to boiling, mixed with calcium chloride in excess, and allowed to stand for an hour or two. The precipitate is washed with hot water, and either weighed as calcium oxide after strong ignition, or decomposed by sulphuric acid and the liberated oxalic acid estimated by permanganate.

(b) *Volumetrically* by permanganate.

#### Phosphoric acid.

(a) As *magnesium pyrophosphate*,  $\text{Mg}_2\text{P}_2\text{O}_7$ .

The operation is conducted as in the estimation of magnesium. If magnesium sulphate is used as the precipitant, the precipitate may be contaminated with basic magnesium sulphate; it is therefore advisable to employ a solution of the chloride, which is made as follows: 85 grams crystallised magnesium sulphate is dissolved in boiling water, acidified with 5 c.c. of hydrochloric acid, mixed with an aqueous solution of 82 grams crystallised barium chloride, boiled, and filtered. Add a few drops of magnesium sulphate solution to be sure that there is no excess of barium, then 165 grams pure ammonium chloride, and 260 c.c. of ammonia, and dilute to 1 litre. Allow to stand two or three days, and filter. In many cases the phosphoric acid is first separated by ammonium molybdate (*v. Methods of Separation*).

(b) *Volumetrically* by uranium nitrate (*v. MANURE*).

#### Silicic acid.

(a) As silica  $\text{SiO}_2$ . Soluble silicates are acidified with hydrochloric acid and evaporated to complete dryness; moistened with strong hydrochloric acid, again evaporated to dryness, the residue treated with dilute acid, and the insoluble silica washed with hot water and ignited.

*Insoluble silicates* are very finely powdered, intimately mixed with about five times their weight of a dry mixture of sodium and potassium carbonates in equal proportions, and heated to redness in a platinum crucible for half an hour. The cooled mass is treated with water, acidified with hydrochloric acid, and evaporated as above.

For the separation of silica when the alkalis have to be estimated, *v. Methods of Separation*, Group VI.

#### Sulphides *v. Hydrosulphuric acid*.

##### Sulphuric acid.

(a) As barium sulphate  $\text{BaSO}_4$  by precipitation with barium chloride. The chief difficulty arises from the tendency of the barium sulphate to separate in a finely-divided condition and to carry down impurities, especially in presence of nitrates and potassium salts. These sources of error are avoided by taking care that the solution is somewhat dilute, is free from nitrates, and contains a moderate but not excessive quantity of free hydrochloric acid. The solution and the barium chloride solution should both be heated to boiling, and mixed *gradually, with continual agitation*. The liquid may be filtered as soon as it has become clear, and the precipitate is washed with hot water and heated to dull redness. If too little hydrochloric acid is present, the precipitate is liable to be impure; if a very large excess of the acid is present, precipitation is not quite complete.

(b) *Volumetrically* by barium chloride (Wildestein, *Fr. I*, 323 and 432).

##### Sulphurous acid.

(a) *Volumetrically* by iodine solution.

(b) *Indirectly* as barium sulphate after oxidation by bromine water, excess of bromine being expelled by boiling.

##### Thiosulphuric acid.

(a) *Volumetrically* by iodine solution.

(b) *Indirectly* as barium sulphate after oxidation by bromine water, excess of bromine being expelled by boiling.

**Water** is usually estimated by difference. If a direct determination is required, the method to be adopted will depend upon circumstances. In many cases it is sufficient to heat the substance on a watch-glass, or in a crucible in a drying oven, at a definite temperature, until the weight is constant. During weighing the dried substance must be carefully protected from the air. Attention must, however, be paid to the possibility of the volatilisation of substances other than water. Many hydrated haloid salts, for example, lose part of their acid. In such cases the substance is previously mixed with a known weight of perfectly dry lead monoxide. Ammonia, ammonium salts, and volatile organic matter may also be given off. If the drying is conducted in a glass tube the vapours may be led into standard acid and the ammonia determined by titration: the total loss, minus the ammonia, gives the amount of water. Some substances increase in weight in consequence of oxidation. Frequently it is desirable to collect the evolved water and weigh it directly. The substance is introduced into a glass tube (plain, or with a bulb in the middle) drawn out and bent at right angles at one end, which passes directly, without any intervening indiarubber tube, through the cork of a U-tube containing either calcium chloride or pumice moistened with strong sulphuric acid (*v. ORGANIC ANALYSIS*). The U-tube is weighed before and after the experiment, and the increase in weight gives the amount of water. It is connected with some form of aspirator, a second drying-tube being interposed to protect the absorption-tube from the water vapour in the aspirator. The opposite end of the glass tube containing the substance is connected with a U-tube filled with a hygroscopic substance to dry the air which enters the apparatus; if the water is absorbed by calcium chloride, the air must be dried by calcium chloride; if it is absorbed in sulphuric acid, the air must be dried by means of pumice moistened with this acid. The substance is carefully heated, and a slow current of air is drawn through the apparatus. Silicates and some other minerals can only be rendered anhydrous by prolonged ignition at a high temperature. Under these conditions carbonic anhydride will likewise be expelled, and the substance may also oxidise.

#### METHODS OF SEPARATION.

In this section the metals are arranged in groups, following the order in the section on Qualitative Analysis. Most of the methods employed for group separations in qualitative analysis are also available for quantitative purposes if certain precautions are observed.

**GROUP I.**—*Silver and mercury* (as mercurous salts) are readily separated from the metals of the succeeding groups by precipitation as chlorides by hydrochloric acid or sodium chloride. The precipitation of lead is not complete, and this metal should be separated in the form of sulphate.

*Lead from silver and mercury.* The lead is separated as sulphate, or the mixture of the three chlorides obtained by precipitation with hydrochloric acid or sodium chloride is repeatedly

treated with hot water until all lead is dissolved. Silver chloride is not quite insoluble in water.

*Silver from mercury.* The mercury is converted into a mercuric salt by treatment with chlorine, aqua regia, or hydrochloric acid and potassium chlorate, and excess of acid or chlorine is expelled by evaporation. The silver is precipitated as chloride, whilst mercuric chloride remains in solution.

*Lead* is separated from all metals of the first four groups by conversion into sulphate; but when other metals are present the use of alcohol is rarely permissible (*v. Lead*).

*Lead from barium.* The two metals are converted into sulphates and the mixture digested with a concentrated solution of sodium thiosulphate at a temperature not exceeding 60°. Lead sulphate dissolves, and can be precipitated in the form of sulphide. Barium sulphate remains undissolved.

*Thallium* from all metals which form soluble iodides by heating with sulphurous acid to ensure reduction to thallous salts, and then precipitating with potassium iodide.

*Thallium from copper.* The solution is precipitated with potassium iodide in presence of sulphurous acid, and the mixture of cuprous and thallous iodides is treated with dilute ammonia. Cuprous iodide dissolves with absorption of atmospheric oxygen; thallous iodide remains undissolved.

GROUP II.—The metals of this group are separated from the metals of the succeeding groups by hydrogen sulphide (*v. General Methods of Estimation, I.*).

*Antimony, arsenic, and tin from the remaining metals of the group.* The well-washed precipitate is digested with a somewhat concentrated solution of yellow ammonium sulphide at a temperature of about 80°. The undissolved portion is allowed to settle, the clear liquid decanted off, and digestion repeated three or four times. Antimony, arsenic, and tin sulphides dissolve; the other sulphides of the group are insoluble. Copper sulphide is slightly soluble in ammonium sulphide, and hence when copper is present sodium or potassium sulphide should be used. Mercuric sulphide, however, dissolves in sodium or potassium sulphide, and in presence of this metal ammonium sulphide must be used.

The sulphides of gold, platinum, iridium, and molybdenum, and selenium, are also soluble in alkaline sulphides.

*Arsenic from antimony and tin.* The solution of the three metals in an alkaline sulphide is diluted, mixed with a large excess of sulphurous acid solution, and boiled until all sulphur dioxide is expelled and the liquid is reduced to two-thirds its original volume. Arsenic sulphide is dissolved; tin and antimony sulphide are insoluble. Wash the insoluble portion with hot water, or, if tin sulphide is present, with a strong solution of sodium chloride and finally with a solution of ammonium acetate, but the latter must not mix with the filtrate.

*Tin from antimony and arsenic.* All tin must be in the stannic condition. The solution of the three metals is mixed with oxalic acid in the proportion of at least 20 grams of acid to each gram of tin present, the solution being so concentrated that the acid will crystallise out on

cooling. The liquid is heated to boiling, treated with a current of hydrogen sulphide for twenty minutes, and filtered. Antimony and arsenic are precipitated; tin remains in solution. The filtrate is mixed with yellow ammonium sulphide until the precipitate which first forms is redissolved, acidified with *acetic acid*, allowed to stand in a warm place for some time, filtered, and the precipitated stannic sulphide washed with a solution of ammonium nitrate and converted into oxide by ignition. F. W. Clarke, to whom this method is due, states that the trace of tin carried down by the antimony and arsenic sulphides is negligible. In accurate work the precipitate is redissolved in an alkaline sulphide, mixed with excess of oxalic acid, and again heated to boiling and treated with hydrogen sulphide to obtain the last traces of tin. According to Fresenius, this second operation should never be omitted. Carnot (C. R. 103, 258) has proposed a very similar method, in which sodium thiosulphate is used in place of hydrogen sulphide.

*Arsenic from other metals.* If the solution is mixed with ferrous chloride and distilled, the arsenic volatilises completely as chloride, which can be collected in the distillate (E. Fischer). This method is especially useful when the arsenic is present in small quantity; if present in large quantity, prolonged distillation is required.

*Gold from all other metals* by reduction of an acid solution by oxalic acid or sulphurous acid.

*Selenium from metals* by reduction with sulphurous acid in hydrochloric acid solution.

*Mercury, copper, cadmium, bismuth, silver, and lead from one another.* The dilute solution is mixed with sodium carbonate and potassium cyanide in excess and heated gently for some time. Lead and bismuth carbonates are precipitated. The solution is acidified with nitric acid and heated until all cuprous cyanide redissolves. Silver cyanide is precipitated. The filtrate is neutralised with sodium carbonate, mixed with excess of potassium cyanide, and treated with hydrogen sulphide. Mercury and cadmium are precipitated; copper remains in solution.

*Bismuth from all metals of the second group except antimony and all the remaining metals except iron.* Nearly neutralise with potash, soda, or ammonia, add ammonium chloride if the metals are not present as chlorides, and a large quantity of water. Allow to stand for some time and ascertain if precipitation is complete by adding more water to a portion of the clear liquid. Dry at 100° and weigh as bismuth oxychloride, BiOCl, or, better, reduce with potassium cyanide and weigh as metal.

*Mercury from copper, bismuth, cadmium, and silver.* Treat the thoroughly washed precipitate of the mixed sulphides with boiling dilute nitric acid; mercuric sulphide is insoluble, the other sulphides dissolve.

*Copper from other metals* as cuprous thio-cyanate (*v. Determination of Metals and Acid Radicles, p. 123*).

*Copper from cadmium.* The mixed sulphides are thoroughly washed and boiled with dilute sulphuric acid (1:5). Cupric sulphide is insoluble, but cadmium sulphide dissolves completely.



GROUP III.—The metals of this group are separated from those of the succeeding groups by precipitation with ammonia in presence of ammonium chloride (*v. General Methods of Estimation*).

*Iron, aluminium, chromium, uranium, beryllium and cerium, from zinc, manganese, nickel, cobalt.* The solution, which must contain iron and uranium as ferric and uranic salts, is nearly neutralised, mixed with excess of finely divided and recently precipitated barium carbonate, and allowed to remain in a closed vessel at the ordinary temperature for some hours with occasional agitation. In presence of nickel and cobalt, ammonium chloride should be added to prevent precipitation of traces of these metals. Filter and wash with cold water. The precipitate contains ferric, chromic, aluminium, beryllium, ceric or uranic hydroxides, mixed with barium carbonate; the filtrate contains the other metals together with some barium. In both cases the barium can be removed by means of sulphuric acid.

*Iron and aluminium from zinc, manganese, nickel, cobalt, uranium, and metals of the succeeding groups.* The solution, which must contain iron as a ferric salt, is nearly neutralised by sodium or ammonium carbonate. In presence of iron the liquid becomes deep red, but no precipitate must be formed. Sodium, or, better, ammonium acetate, is added in sufficient but not excessive quantity, and the liquid is boiled until the precipitate becomes granular and settles rapidly. Prolonged boiling makes the precipitate slimy. The liquid is filtered whilst hot, and the precipitate is washed with hot water; if the liquid is allowed to cool the precipitate is partially redissolved. The precipitate is converted into ferric and aluminium oxides by ignition; the other metals are in the filtrate. It is advisable, and in presence of nickel essential, to redissolve the precipitate and repeat the process. This method is not available for the separation of chromium.

The same result can be obtained with ammonium formate or succinate.

*Aluminium and chromium from iron, zinc, manganese, nickel, and cobalt.* Mix the solution with a moderate quantity of pure normal potassium tartrate, then with pure potash or soda until the precipitate redissolves, add ammonium sulphide in slight excess and allow to stand. Wash the precipitate with water containing ammonium sulphide. Aluminium and chromium are in the filtrate, the other metals in the precipitate. If iron and chromium are absent, it is sufficient to add the alkaline tartrate, excess of ammonia, ammonium chloride and ammonium sulphide.

*Iron from chromium and aluminium.* The three metals are weighed together as oxides. The precipitate is then finely powdered, an aliquot portion is placed in a porcelain boat and heated to redness in a current of hydrogen until no further reduction takes place, allowed to cool completely in the hydrogen and again weighed. The loss of weight represents the oxygen in the ferric oxide, and from this the quantity of iron is readily calculated. This method is especially valuable for small quantities of iron. The boat is inclosed in a well-corked tube while weighing.

Chromium is readily separated from many metals, *e.g.* aluminium, by conversion into chromate, which is not precipitated by alkalis. This can be done in one of the following ways. (a) Evaporate nearly to dryness, add strong nitric acid, heat, and add crystals of potassium chlorate from time to time until the chromium is completely oxidised. (b) Nearly neutralise with sodium carbonate, add sodium acetate in excess, pass a current of chlorine into the liquid or add bromine, and heat. The chromium is rapidly oxidised to chromate, especially if sodium carbonate is added from time to time to keep the liquid nearly neutral. (c) Make the solution alkaline with potash or soda, saturate with chlorine and then heat to expel excess of gas, and decompose hypochlorites by heating with ammonia.

*Aluminium from chromium.* After chromium has been converted into chromic acid, the aluminium may be precipitated as hydroxide or as phosphate (*v. Determination of Metals*). The filtrate is acidified, heated to boiling, and sodium thiosulphate added until the chromium is completely reduced; it can then be estimated as phosphate in the same way as aluminium.

*Uranium* is separated from the other metals of this group by the solubility of its hydroxide, acid uranates, and sulphide, in ammonium carbonate.

*Beryllium* is separated by means of barium carbonate, and also by the solubility of its carbonate in ammonium carbonate, from which it is precipitated on boiling.

*Beryllium from aluminium.* The solution, which should not measure more than 200 c.c., is mixed with excess of potassium hydroxide purified by means of alcohol, and heated to boiling in a platinum dish for about twenty minutes. It is then diluted with hot water, and the precipitated beryllium oxide is filtered off and washed with hot water. If the original solution is too dilute, some alumina is also precipitated on boiling (Zimmermann, *Fr.* 1888, 61).

*Cerium* is separated from other metals by saturating the solution with sodium sulphate by adding the salt in fine powder. A crystalline double sulphate of cerium and sodium separates and is washed with a saturated solution of sodium sulphate.

GROUP IV.—Metals of this group are separated from those of the succeeding groups by means of ammonium sulphide (*General Methods of Estimation*, I.).

*Nickel and cobalt from zinc and manganese.* The neutral solution is heated to boiling and precipitated with a boiling solution of sodium sulphide. The precipitate, which is dense and granular, is well washed and treated with cold dilute hydrochloric acid. Zinc and manganese dissolve, but nickel and cobalt sulphides precipitated under these conditions do not dissolve.

*Nickel from cobalt.* The solution, which should contain but little free acid, is mixed with excess of pure potassium cyanide free from cyanate (the ordinary cyanide is fused with charcoal, dissolved in water, filtered, and evaporated in a silver dish), heated to boiling and mixed with a solution of mercuric oxide in mercuric cyanide. The precipitate, when washed, dried, and ignited, leaves a residue of nickel oxide, NiO, which is

weighed. Cobalt is usually determined by difference; but if direct estimation is required, the filtrate from the nickel is evaporated to dryness, heated for some time with strong sulphuric acid, and the cobalt estimated in the solution.

*Zinc, cobalt, and nickel from manganese (and uranium).* The solution is nearly neutralised, mixed with excess of sodium acetate and a small quantity of acetic acid, heated to boiling, and a brisk current of hydrogen sulphide passed into the boiling liquid for half an hour. Manganese (and uranium) remain in solution, and the former can be precipitated by sodium carbonate. The precipitate contains nickel, cobalt, and zinc. It is dissolved in hydrochloric acid and potassium chlorate, excess of acid expelled, pure potassium cyanide added in excess, and then sodium sulphide so long as white zinc sulphide is precipitated. Nickel and cobalt remain in solution.

*Zinc from nickel and cobalt.* Add excess of pure potassium cyanide and precipitate the zinc with sodium sulphide as in the preceding method.

GROUP V.—The metals of this group are separated from those of the following group by precipitation with ammonium carbonate (*v. General Methods of Estimation*). The liquid is first made alkaline with ammonia and afterwards heated to boiling to ensure complete precipitation.

*Barium from calcium and strontium.* The dilute neutral or feebly acid solution is mixed with excess of freshly prepared hydrofluosilicic acid and one-third its volume of alcohol of 95 per cent., allowed to stand twelve hours, collected on a weighed filter, washed with a mixture of equal parts of water and alcohol, and dried at 100°. Calcium and strontium are not precipitated.

*Barium and strontium from calcium.* The solution is mixed with a concentrated solution of ammonium sulphate, using 50 parts of the latter salt for one part of the mixed salts, heated to boiling with addition of a small quantity of ammonia, and the precipitate washed with water containing ammonium sulphate. The filtrate contains the calcium, which can be precipitated by ammonium oxalate.

*Calcium from strontium.* Convert the metals into nitrates, evaporate to dryness, and extract with a mixture of equal volumes of alcohol and ether, which dissolves calcium nitrate but not strontium nitrate.

*Calcium from magnesium.* The calcium is precipitated by ammonium oxalate (*v. Determination of Metals*), adding sufficient of this salt to convert both metals into oxalates, since calcium oxalate is appreciably soluble in a solution of magnesium chloride. In very accurate separations the precipitate should be filtered off, redissolved in hydrochloric acid, and reprecipitated by adding excess of ammonia and a small quantity of ammonium oxalate.

GROUP VI.—*Magnesium from alkalis.* The magnesium is precipitated with ammonium phosphate in the usual way, the filtrate evaporated to dryness, heated to expel ammonium salts, the residue evaporated two or three times with strong nitric acid to remove hydrochloric acid and the phosphoric acid removed by stannic oxide (*v. Phosphoric acid from metals*).

*Alkalis from magnesium.* (a) The solution is made distinctly alkaline with pure milk of lime (calcium hydroxide suspended in water) and boiled for some time, care being taken that it remains alkaline. The liquid is filtered, made alkaline with ammonia, and the calcium precipitated by adding ammonium carbonate and a small quantity of ammonium oxalate. The filtrate is acidified with hydrochloric acid and evaporated in a weighed platinum dish, heated to expel ammonium salts, and the alkaline chlorides weighed. They should dissolve completely in water and should give no precipitate when mixed with ammonium carbonate and allowed to stand for some time. If any calcium is present it must be removed by repeating the treatment with ammonium carbonate and oxalate.

(b) The solution, which must contain only potassium, sodium, and magnesium, is mixed with excess of oxalic acid, evaporated to dryness, and the oxalic acid expelled by heating carefully over a lamp until white fumes cease to come off. The residue is treated with water, when potassium and sodium dissolve as carbonates, whilst magnesium oxide remains undissolved.

*Alkalis from silicates.* The finely powdered silicate (1 gram) is mixed intimately with an equal weight of ammonium chloride and eight parts of dense granular calcium carbonate, and heated to redness for half an hour. The product is boiled with water in a platinum or silver dish for two hours, care being taken to make up the loss by evaporation, and the liquid is filtered and the residue well washed with hot water. The filtrate, which contains calcium and the alkalis, is treated in the manner just described. In this method of decomposition, which is due to J. Lawrence Smith, the silicate is decomposed by the calcium oxide which is dissolved by the fused calcium chloride formed by the action of the ammonium chloride on the calcium carbonate.

*Potassium from sodium.* The metals are converted into chlorides, which are evaporated to dryness and weighed together after drying at 150°. The salts are dissolved in water, mixed with platinic chloride in sufficient quantity to convert both into platinochlorides, and evaporated nearly but not quite to dryness. The residue is then treated with alcohol, which dissolves the sodium but not the potassium salt (*v. Potassium*). If the mixture is evaporated to complete dryness and heated so that the sodium platinochloride becomes anhydrous, it dissolves with difficulty in alcohol. Under some conditions reversion takes place and sodium chloride separates in white crystals insoluble in alcohol. In this case the alcohol is very carefully evaporated and the residue again treated with platinic chloride.

In order to separate small quantities of potassium from large quantities of sodium, advantage may be taken of the fact that potassium chloride is more soluble than sodium chloride in strong hydrochloric acid (Fr. 1880, 156). The dry mixed chlorides are thoroughly moistened with concentrated hydrochloric acid, 2 c.c. of the acid is then added, and the salt thoroughly crushed and stirred with a glass rod. After standing for a few minutes the acid is poured off into a small dish. Ten repetitions of this treatment, using 2 c.c. of acid each time, will



suffice to remove all potassium, whilst the greater part of the sodium chloride is not dissolved. The acid solution is evaporated to dryness and the potassium determined as platinumchloride (C. J. 39, 506). By adopting this plan much less platonic chloride is required, and the separation is much more accurate.

*Ammonium salts* can be removed from a solution in two ways—(1) by evaporating to dryness and carefully heating over a lamp until all fumes cease to come off. (2) By concentrating the solution and heating for some time with excess of strong nitric acid. When evolution of oxides of nitrogen ceases, the liquid is evaporated to complete dryness and the nitrates converted into chlorides by repeated treatment with hydrochloric acid if necessary.

#### Acid Radicles.

*Bromine from chlorine.* The two elements are precipitated by excess of silver nitrate and weighed together. The filter ash is removed, the precipitate cautiously heated to fusion, and a portion poured into a weighed porcelain boat. The boat is again weighed, heated to fusion in a current of dry chlorine in a glass tube until all bromine is expelled, and the silver chloride formed is weighed. It is advisable to heat in chlorine for a further period of ten minutes and weigh again. The loss of weight multiplied by 4.223 gives the amount of silver bromide in the weight of precipitate treated with chlorine, from which the quantity in the whole precipitate is readily calculated (*v. Indirect Methods of Determination*).

This method gives accurate results if the proportion of bromine is not too small. When a small quantity of bromine is mixed with a large quantity of chlorine, the former may be concentrated by taking advantage of the fact that if a limited quantity of silver nitrate is added the precipitate will contain all the bromine, but only a portion of the chlorine. In one portion of the substance the two elements are determined together by complete precipitation. Another portion in somewhat dilute solution is mixed with a quantity of silver nitrate insufficient for complete precipitation and allowed to stand in the cold for some time with repeated agitation. The precipitate is collected, washed, and weighed, and the proportion of bromine determined in the manner already described. The quantity of silver nitrate which should be used depends upon the relative proportions of chlorine and bromine. If one part of bromine is present for every 1,000 parts of chlorine, one-fifth or one-sixth of the silver necessary for complete precipitation should be used; if one part to 10,000, only one-tenth; if one part to 100,000, only one-sixtieth (Fehling).

*Iodine from chlorine* in exactly the same way as bromine from chlorine. The loss of weight on treating with chlorine, multiplied by 2.569, gives the weight of silver iodide in the portion of precipitate taken.

*Iodine from chlorine or bromine.* The solution is slightly acidified with hydrochloric acid, mixed with palladium chloride until precipitation is complete, and allowed to stand in a warm place for twenty-four or forty-eight hours. The precipitate of palladium iodide  $\text{PdI}_2$  is collected on a weighed filter, washed with

warm water, and dried at  $100^\circ$ , or is reduced by heating in hydrogen and the metal weighed.

*Iodine* can also be liberated by nitrous acid and estimated volumetrically (*v. Volumetric Methods*).

*Bromine, chlorine, and iodine from one another.* The three elements are precipitated and weighed together in one part of the solution. In another part the iodine is separated as palladium iodide by palladium chloride, or better, nitrate; the excess of palladium is removed by hydrogen sulphide and excess of the latter by ferric sulphate; and the chlorine and bromine in the filtrate are precipitated completely or fractionally and the bromine determined in the manner previously described. The chlorine is estimated by difference.

Several indirect methods of estimating these three elements in a mixture have been proposed. They are based on the methods given, together with the fact that the radicles may be precipitated exactly by a standard solution of silver nitrate and the precipitate weighed, the proportion of silver and haloids in the precipitate being thus determined (*v. Fresenius, Quantitative Analysis, sect. 5*).

*Oxalic acid from phosphoric acid.* The solution is neutralised if necessary, then acidified with acetic acid and the oxalic acid precipitated as calcium oxalate.

*Phosphoric acid from metals.* (a) The nitric acid solution, as free as possible from hydrochloric acid, and free from silicic and arsenic acids, is mixed with excess of a solution of ammonium molybdate in nitric acid, boiled for a few minutes, and filtered after standing for a short time. The precipitate is washed with dilute nitric acid, dissolved in ammonia, and the phosphoric acid precipitated by magnesia mixture. This method is more especially applicable when the quantity of phosphoric acid is relatively small. To prepare ammonium molybdate solution, 25 grams of the salt is dissolved in 100 c.c. of dilute ammonia and the solution poured gradually with constant and vigorous agitation into 500 c.c. of a mixture of 3 vols. strong nitric acid and 1 vol. water. The liquid is heated at  $50^\circ$  for some time and the clear solution drawn off.

(b) By stannic oxide. The nitric acid solution is concentrated, mixed with fuming nitric acid boiling at  $86^\circ$ , heated gently, and granulated tin added gradually in quantity not less than four times the amount of phosphoric acid present. The stannic oxide produced forms an insoluble compound with the phosphoric acid. This is filtered off, washed with hot water, dissolved in potash, the solution saturated with hydrogen sulphide, acidified with acetic acid, and the stannic sulphide filtered off. This filtrate is concentrated, any stannic sulphide which separates is removed, and the phosphoric acid is estimated in the usual way (Reynoso). The original filtrate from the stannic oxide contains the metals previously combined with the phosphoric acid.

(c) The nearly neutral solution is mixed with silver nitrate and digested for some time with excess of silver carbonate. The phosphoric acid separates as silver phosphate, the metals remain in solution with the excess of



silver nitrate. The silver is removed by hydrochloric acid.

(d) When the phosphoric acid is combined with metals which form phosphates insoluble in water but soluble in acetic acid, the solution is nearly neutralised, mixed with sodium or ammonium acetate, and a slight excess of ferric chloride containing a known weight of iron added. The liquid is heated to boiling, the mixture of ferric phosphate and basic acetate washed with hot water, dried, and heated in a platinum crucible until the weight is constant. The weight of the precipitate minus the known weight of the ferric oxide gives the phosphoric anhydride  $P_2O_5$ . The precipitate may be moistened with nitric acid before the final ignition.

*Silicic acid from titanio acid.* The silica and titanium dioxide are weighed together, the mixture fused with a somewhat large quantity of potassium hydrogen sulphate, and the cooled mass extracted with water. Silica is left undissolved, titanio oxide dissolves, and can be precipitated from the filtrate by ebullition (*v. Titanium*).

*Sulphides.* If the sulphides are decomposed by hydrochloric acid the hydrogen sulphide is absorbed in hydrochloric acid containing bromine (*v. Determination of Metals*). Insoluble sulphides are decomposed by gently heating with aqua regia or with hydrochloric acid and bromine, and the sulphuric acid estimated in the solution. This latter method gives the total sulphur.

*Sulphuric acid from all other acids except hydrofluosilicic* by precipitation with barium chloride in presence of hydrochloric acid.

*Sulphuric acid from hydrofluosilicic acid.* The solution is mixed with excess of potassium chloride and an equal volume of strong alcohol, filtered through a weighed filter, and the precipitate of potassium silicofluoride ( $K_2SiF_6$ ), washed with a mixture of equal volumes of alcohol and water, and dried at  $100^\circ$ . The sulphuric acid in the filtrate is estimated in the usual way after expulsion of the alcohol.

*Titanic acid from silicic acid* (*v. Silicic acid from titanio acid*).

#### ELECTROLYTIC ESTIMATION OF METALS.

It is well known that when an electric current is passed through solutions of metallic salts, the latter are decomposed with liberation of the metal at the kathode or negative electrode, and the acid radiate at the anode or positive electrode. In some cases the metal is not obtained in the free state owing to its action on the solvent, in a few others it separates at the positive pole in the form of peroxide. In order that the decomposition may be available for quantitative estimations it must not be complicated by secondary reactions; the metal must be deposited in a pure condition and must be so compact and so firmly adherent to the electrode that it can be washed, dried, and weighed without loss. When these conditions are fulfilled, estimations by electrolysis are simple, accurate, and require but little attention. Many determinations can be made simultaneously, and in several cases small quantities of metals can be separated and estimated with a degree of accuracy not readily attainable by other methods.

Most of the methods of electrolytic estimation are due to A. Classen (*Quantitative chemische Analyse durch Electrolyse*, 2nd ed. Berlin, 1886, translated by W. Herrick, New York, 1887). The accuracy of an electrolytic separation depends mainly on the strength of the current and the form in which the metal is present. Chlorides are unsuitable because of the action of the liberated chlorine on the positive electrode, nitrates are available in a few cases; sulphates are more generally available, but the soluble double salts formed by the union of the oxalates of the heavy metals with ammonium or potassium oxalate are found to have special advantages. With a suitable strength of current the metals are deposited in a very dense and pure condition, and only carbonic anhydride is liberated at the anode.

*Batteries and Resistances.*—Only those batteries are suitable which will give a fairly constant current for several hours. For feeble currents Daniell or Meidinger cells answer very well; for strong currents Grove's or Bunsen cells must be used. The newer forms of bichromate battery in which the zinc is inclosed in a porous cell are also suitable. A Clamond or Noë thermoelectric battery may be employed, but they soon deteriorate, and even at the best yield only very weak currents. A continuous current dynamo of the Siemens-Halske or any similar type is very convenient when large numbers of determinations have to be made.

In order to regulate the current it is necessary to be able to introduce or remove from the circuit resistances of definite magnitude. An ordinary rheostat or a resistance box answers every purpose, but if it is exposed to the air of the laboratory it is advisable to make the connections by means of mercury contained in small cups, and not by ordinary metal plugs, which readily corrode. Classen uses a glass tube 22 cm. long and 8.5 cm. diameter, filled with a cold saturated solution of zinc sulphate. One end of the cylinder is closed by a zinc plate connected with the wire from the battery, the other end is closed by a cork through which passes a zinc rod to which is attached a circular zinc plate of the same diameter as the tube. The rod is connected with the other wire of the circuit, and the resistance is increased by separating the zinc plates and reduced by bringing them close

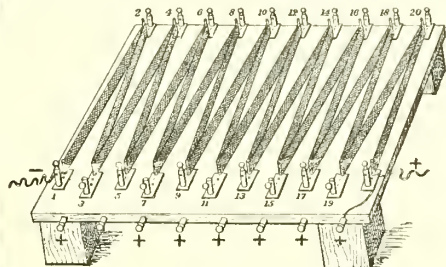


FIG. 10.

together. Classen has recently described (*B.* 21, 360) a rheostat by means of which several currents of different intensities may be obtained from one battery. It consists essentially of a rectangular wooden board with a row of brass

pegs and binding screws down one side and a similar row on the opposite side. The resistance is obtained by means of German-silver wire-gauze, a strip of which is attached to one of the corner binding-screws and is then carried backwards and forwards across the board, zigzag fashion, passing round a peg first on one side and then on the other, and ending at a binding screw which is connected with the positive pole of the battery. There is also a row of 8 or 10 binding screws connected by a thick wire with the positive pole only. In making a determination one of the electrodes is connected with one of these positive binding screws and the other with any one of the binding screws attached to the pegs round which the wire gauze passes. The resistance depends of course on the length of gauze through which the current has to pass. A somewhat similar arrangement for use with a dynamo is described in Classen's book, p. 27.

*Measurement of the current.*—The strength of the current is expressed in amperes, an ampère being the current obtained with an electromotive force of one volt and a resistance of one ohm. One ampère corresponds with the liberation of 10·436 c.c. of oxygen and hydrogen per minute from acidulated water, or with the decomposition of 19·69 milligrams of copper or 67·1 milligram of silver per minute.

A *voltameter* consists essentially of a pair of platinum plates immersed in acidulated water

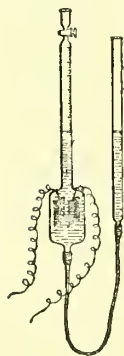


FIG. 11.

and when the volume of the liberated gas is read off the level tube is adjusted so that the liquid is at the same level in both tubes (Classen, B. 21, 364).

The current may also be measured by means of the tangent galvanometer, which consists of a magnetic needle suspended horizontally at the centre of a vertical circular coil of copper wire or sheet copper through which the current passes. The strength of the current is proportional to the tangent of the angle of the deflection of the needle. The galvanometer is calibrated by inclosing it in the same circuit with a voltameter, and observing the angle of deflection corresponding with a given volume of gas per minute. If  $V$  is the volume of gas per minute, corrected to standard conditions,  $A$  the corresponding angle of deflection, and  $R$  the reduction factor for the galvanometer,  $R = \frac{V}{\tan A}$ , and if a current

giving one c.c. of mixed oxygen and hydrogen per minute is taken as a special unit of current, then for any other angle of deflection  $A$  the strength of the current  $I$  is given by the expression,  $I = R \tan A$ .

Miller's ampère-meter, which gives the strength of the current directly in amperes and fractions of an ampère, is a compact and convenient instrument for measurements of this kind (v. Stewart and Gee's Practical Physics, Part II.).

*Apparatus and manipulation.*—The anode consists of a well-polished (not hammered) platinum dish about 9 cm. diameter and 4 cm. deep, with a capacity of about 220 c.c. It should weigh from 35 to 40 grams. The anode is a disc of thick sheet platinum 4·5 cm. diameter, to the centre of which is fastened a thick vertical platinum wire. The dish may be covered with a cover-glass through which a hole has been bored for the passage of the anode. The stand consists of a stout glass rod fixed in a heavy base and carrying a brass ring to the boss of which is attached a binding screw. The ring supports the dish and has three contact points of platinum riveted to it. The anode is attached to a binding screw at the end of a brass rod which is carried by the same stand, the boss of the rod being provided with another binding screw for making contact with the battery. Malapert (Fr. 1887, 56) has described a form of stand which is very convenient when several determinations have to be conducted simultaneously.

The Luckow or Mansfeld kathode consists of a cylinder or cone of sheet platinum, open at the top and bottom, and riveted to a



FIG. 12.

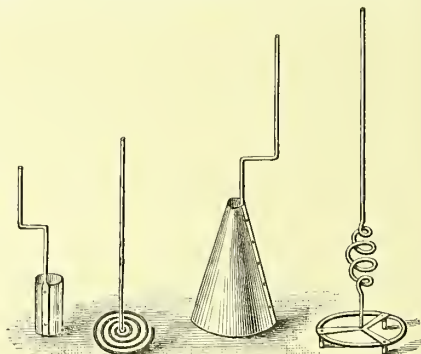


FIG. 13.

stout platinum wire. The anode is a flat spiral of thick platinum wire, from the centre of which the wire rises vertically. The electrodes are supported in a tall beaker, of not much greater diameter than the kathode, by means of a stand similar to that just described, the flat spiral being below the cone or cylinder, whilst the vertical wire from the spiral passes up through its centre.

If the quantity of liquid is small, a platinum crucible may serve as the kathode, the anode consisting of a smaller crucible with the bottom removed and a few lenticular openings in the

sides to facilitate the circulation of the liquid. The anode is suspended inside the kathode by means of a platinum wire, care being taken that they do not touch.

In many cases the deposition of the metal may be greatly accelerated by heating the liquid, but the temperature should never exceed  $80^{\circ}$ . Before stopping the current it must be ascertained that precipitation is complete by withdrawing a small quantity of the liquid by means of a capillary tube and testing with some delicate and characteristic reagent, e.g. potassium ferrocyanide for copper, hydrogen sulphide for lead. The liquid is then poured off and the metal washed, first with water, then with alcohol, and finally with ether, and dried at  $100^{\circ}$ . Whenever deposition takes place in an acid solution, the liquid must be removed and the metal washed whilst the current is passing, in order to prevent re-solution of a small quantity of the metal. This is readily effected by draining off the contents of the dish by means of a siphon, whilst water is run in from a beaker by means of a precisely similar siphon, so that the dish remains full of liquid whilst the washing is proceeding. Beakers with a lateral tubulus near the top are very convenient (Malapert).

*Reagents.*—Ammonium and potassium oxalates not unfrequently contain lead and iron, which are removed by mixing the hot saturated solutions with a slight excess of ammonium sulphide, boiling and filtering. The excess of ammonium sulphide is decomposed by a current of air, the liquid again filtered, and the salt recrystallised.

Oxalic acid contains the same impurities, and is purified by repeated recrystallisation.

Ammonium sulphate is purified in the same way as the oxalate.

Sodium sulphide must be free from hydroxide or polysulphides. It is prepared by saturating sodium hydroxide solution with hydrogen sulphide, and filtering with as little exposure to air as possible. The filtrate is rapidly evaporated until crystals begin to separate, and is then poured whilst hot into small flasks or bottles with well-fitting glass stoppers, which should be made perfectly air-tight by means of paraffin.

Alcohol and ether used for washing the metal must be nearly absolute, free from any trace of acidity, and must leave no residue on evaporation. They should be allowed to stand over quicklime for at least 24 hours, and then be distilled on a water-bath.

#### *Estimations.*

The volume of the solution should be 150–200 c.c. and it should contain not more than 0.5 to 0.6 gram of metal. The quantity of ammonium or potassium oxalate required is from 3 to 5 grams in ordinary cases. The strength of the current is expressed in c.c. of electrolytic gas per minute according to Classen's data.

**Aluminium** is precipitated in the form of hydroxide by the carbonate formed from the oxalate during electrolysis, but precipitation does not take place so long as a considerable quantity of the oxalate remains undecomposed. Uranium behaves in a similar manner, but the precipitate redissolves in excess of ammonium

carbonate. Beryllium likewise remains in solution if the liquid is not heated. Chromium is converted into ammonium chromate.

**Antimony** is not satisfactorily precipitated from the oxalate or tartrate, but can be accurately deposited from a solution of the sulphide in ammonium hydrosulphide free from ammonia or polysulphides. The best results are obtained by adding 10 c.c. of a saturated solution of sodium monosulphide to 100–150 c.c. of solution which should not contain more than 0.16 gram of antimony; current 1.5–2.0 c.c. of gas per minute. Polysulphides hinder or even prevent precipitation, and must be removed by cautiously adding hydrogen peroxide and heating the liquid until it just becomes colourless.

**Arsenic** cannot be separated quantitatively.

**Beryllium v. Aluminium.**

**Bismuth** from a solution of the double ammonium oxalate; current about 0.1 c.c. of gas per minute. Some peroxide separates on the anode, but afterwards redissolves. The quantity of bismuth should be small and the kathode should have a large surface, since the metal is not very firmly adherent. Bismuth may also be precipitated from a slightly acid solution of the sulphate, a stronger current being used.

**Cadmium** from a hot solution of the double oxalate (preferably potassium), loss by evaporation being repeatedly made up by addition of water; current 0.2 c.c. of gas per minute. Also from a solution of the nitrate or sulphate containing about 3 grams of sodium acetate per 100 c.c. and a few drops of acetic acid; current about 0.6 c.c. of gas per minute. Also from a solution containing excess of potassium cyanide, with the current from 3 Bunsen cells.

**Chromium v. Aluminium.**

**Cobalt** from a hot solution of the double ammonium oxalate; current, 8 to 10 c.c. of gas per minute. Also, in absence of chlorides, from a cold solution containing, in 200 c.c., 40 to 50 c.c. of ammonia and 5–6 grams ammonium sulphate; current about 5 c.c. of gas per minute.

**Copper** from a solution of the double ammonium oxalate, which should be nearly saturated with the ammonium salt and is heated to  $40^{\circ}$ – $50^{\circ}$ C. The liquid must be kept acid, especially towards the end of the operation, by addition of oxalic acid. If much copper is present the free acid should not be added until most of the metal is precipitated, in order to avoid separation of the insoluble oxalate. With a current giving 3–4 c.c. of gas per minute, precipitation is complete in two or three hours (B. 1888, 2899).

Also from a moderately dilute ammoniacal solution containing 2–3 per cent. of ammonium or potassium nitrate (Rüdorff, B. 1888, 3050).

Also from an acid solution of the sulphate or nitrate. The latter should be free from chlorides and should contain in 200 c.c. about 20 c.c. of nitric acid of sp.gr. 1.21; current 3 to 4 c.c. of gas per minute.

**Gold** from the double potassium cyanide (*v. Silver*). The kathode should be covered with a layer of silver to protect it from the aqua regia which must be used afterwards to dissolve the gold.

**Iron** from a hot solution of the double oxalate, which must contain no nitrates and no free acid. The best results are obtained with a mixture of ammonium oxalate (3 parts) and potas-



sium oxalate (1 part); current 10 to 12 c.c. of gas per minute, increased to 15–20 c.c. towards the end of the operation.

*Iridium v. Platinum.*

Lead as peroxide on the anode from a solution of the nitrate, which in absence of other metals should contain 10 per cent. of free nitric acid, but in presence of other metals a smaller quantity of acid is sufficient; current, a few tenths of a cubic cm. of gas per minute. The peroxide is washed with water whilst the current is passing, and is dried at  $110^{\circ}$ . The anode should have as large a surface as possible, and if the quantity of lead is considerable it is advisable to use the dish as the anode.

Manganese as peroxide on the anode, which should have as large a surface as possible; current 9 to 12 c.c. of gas per minute. Potassium oxalate must be used, since in presence of the ammonium salt precipitation is not complete. The peroxide is converted into  $Mn_2O_4$  by ignition either on the anode, or if necessary after filtration. The manganese is also precipitated as peroxide from a solution containing free sulphuric or nitric acid. The former must be used in presence of metals which would be precipitated by the ammonia resulting from the reduction of the nitric acid.

Mercury from a solution containing free nitric acid; current 0.2–0.5 c.c. of gas per minute. The metal is washed, and dried over sulphuric acid. Smith and Kerr (A. C. J. 8, 207) use a current giving 4 c.c. of gas per minute, deposition being complete in 30–45 minutes. Insoluble mercury compounds are suspended in dilute nitric acid or in a 10 per cent. solution of sodium chloride and electrolysed.

Nickel from the double oxalate in the same way as iron, or from the ammoniacal solution in the same way as cobalt.

Palladium in the same way as platinum.

Platinum from a gently heated solution, containing ammonium or potassium oxalate, or free hydrochloric or sulphuric acid in small quantity; current, one Bunsen cell. Iridium is not deposited under these conditions, a stronger current being required.

Silver from a solution in excess of potassium cyanide; current 1.5 to 2 c.c. of gas per minute. Also from a solution containing one-tenth its volume of nitric acid of sp.gr. 1.2; current 2.0 to 2.5 c.c. of gas per minute.

Thallium v. G. Neumann, B. 21, 356.

Tin from a hot solution of the double ammonium (but not potassium) oxalate, which may contain a small quantity of free acid; current 9 to 10 c.c. of gas per minute. If much tin is present ammonium hydrogen oxalate should be used in place of the normal salt. Also from a solution of the sulphide in ammonium (but not sodium or potassium) sulphide under the same conditions as antimony; current 9–10 c.c. of gas per minute. Any film of sulphur which forms on the surface of the metal may be removed without loss of the latter by washing with alcohol and rubbing gently with the finger moistened with alcohol. Sodium sulphide may be converted into the ammonium salt by heating the liquid with 25 grams of ammonium sulphate, boiling for about 15 minutes, and after cooling adding water to dissolve the sodium sulphate.

Tin may also be separated from a solution of the chloride containing a small quantity of the free acid.

*Uranium v. Aluminium.*

Zinc from the double ammonium oxalate; current 8 to 10 c.c. of gas per minute. The metal seems to alloy with the platinum and injures the surface of the latter. It is therefore desirable to coat the cathode with a layer of copper or silver before using it. Also from a solution of the double cyanide, prepared by adding sodium hydroxide till a precipitate forms and then potassium cyanide till the precipitate dissolves; current, 4 Bunsen cells. The liquid in this case becomes very hot and should be cooled by a water-jacket. Zinc can also be separated from a solution of the sulphate, which is mixed with sodium acetate and acidified with citric acid; current 4 to 5 c.c. of gas per minute.

*Separations.*

The separation of metals by electrolysis is based upon the fact that a certain minimum intensity of current is required to precipitate a given metal, and a current which is sufficient to precipitate some metals, such as platinum or copper, will not precipitate others, such as iron and nickel. Moreover, some metals are precipitated from acid solutions, whilst others are not. The details already given will enable methods of separation to be devised. The following are amongst those most generally useful.

*Antimony from arsenic.* The arsenic is completely oxidised to arsenic acid by aqua regia, the excess of acid expelled, the liquid mixed with 50 c.c. of sodium sulphide solution of sp.gr. 1.22 and a solution of 1 gram of sodium hydroxide, diluted to 200 c.c., and treated as in the separation of antimony and tin.

*Antimony and tin.* The mixed sulphides are dissolved in 60 c.c. of a solution of sodium sulphide of sp.gr. 1.22, mixed with a concentrated solution of 1 gram of sodium hydroxide and allowed to cool completely; current 1.5 to 2.0 c.c. of gas per minute. After 12 hours remove the antimony, convert the sodium sulphide into ammonium sulphide, and separate the tin (v. also B. 1888, 2897).

*Cadmium from zinc.* By precipitation of the cadmium from a warm solution containing a large quantity of potassium oxalate, with a current giving not more than 0.15 c.c. of gas per minute. After separation of the cadmium, the zinc is precipitated by a stronger current. Cadmium may also be precipitated from a solution of the acetate or sulphate acidified with acetic acid, by a current giving 0.5 to 0.6 c.c. of gas per minute.

*Copper from arsenic.* The solution is evaporated on the water-bath two or three times with small quantities of a solution of bromine in hydrochloric acid. The arsenic is completely volatilised as bromide.

*Copper from cadmium, bismuth, and other metals which are not precipitated in nitric acid solutions.* By electrolysis of a solution containing free nitric acid.

*Copper from calcium, barium, &c.* By electrolysis of a solution containing free nitric acid.

*Copper from iron, cobalt, nickel, &c.* By precipitation of the copper from a solution of the double oxalates by a very weak current, and subsequent precipitation of the other metals by a strong current.

*Copper from lead, v. Lead.*

*Copper from silver, v. Silver.*

*Copper from tin.* By treatment of the solution with excess of sodium sulphide. The precipitated copper sulphide is dissolved in nitric acid; the tin is precipitated from the solution of the alkaline sulphide.

*Iron from cobalt.* The metals are precipitated and weighed together, then dissolved in acid and the iron estimated by titration. If permanganate is used the red colour of the cobalt must be masked by adding a solution of nickel in just sufficient quantity to make the liquid colourless.

*Iron from manganese.* The liquid is mixed with a large excess of ammonium oxalate, heated, and electrolysed by a current giving 10–12 c.c. of gas per minute. Even with large quantities of manganese only a very small quantity of the peroxide separates on the anode. If a slight film forms on the iron it is removed by washing with alcohol and rubbing gently with the finger moistened with alcohol. The manganese in the liquid is estimated by precipitation with an oxidising agent.

*Iron from nickel, v. Iron from cobalt.*

*Iron from zinc.* In the same way as iron from cobalt. If the proportion of zinc is more than one-third that of the iron, a known quantity of iron in the form of ferrous ammonium sulphate must be added to the solution.

*Iron, cobalt, nickel, and zinc from manganese, aluminium, chromium, &c.* By electrolysis of a cold solution containing a large proportion of ammonium oxalate; current 10 c.c. of gas per minute. The precipitate is treated with a solution of oxalic acid while the current is passing and the electrolysis is continued for some time. If manganese and chromium are present together, the manganese peroxide afterwards precipitated always contains chromium, it is therefore dissolved in hydrochloric acid and reprecipitated by an alkali and an oxidising agent.

*Lead from cadmium, iron, nickel, and all metals which are not deposited from a solution containing free nitric acid.* By separation as peroxide from an acid solution.

*Lead from copper, silver, and metals which are deposited from acid solutions.* By separation of the lead as peroxide on the anode, and the other metal on the cathode, from a solution containing free nitric acid. If the quantity of lead is at all considerable, it is advisable to use the larger electrode as the anode.

*Manganese from calcium &c.* By precipitation as peroxide from a solution containing free nitric acid.

*Manganese from nickel,* in the same way as from iron.

*Mercury from bismuth, cadmium, and other metals which are not precipitated from acid solutions.* By electrolysis of a solution containing free nitric acid.

*Mercury from iron, nickel, cobalt, &c.* By precipitating the mercury with a weak current,

from 0.2–0.5 c.c. of gas per minute, and the other metals afterwards by a strong current.

*Mercury and silver.* The two metals are precipitated and weighed together, then heated to volatilise the mercury, and the residual silver weighed.

*Silver from all metals which form soluble double oxalates.* By precipitating as silver oxalate with a large excess of a saturated solution of ammonium oxalate, and washing the precipitate with the same solution. The other metals are estimated in the filtrate; the silver oxalate is dissolved in potassium cyanide and electrolysed.

#### VOLUMETRIC METHODS.

In volumetric analysis the proportion of a substance is ascertained, not by separation and weighing, but by determining the exact volume of a reagent solution of definite strength required to produce some particular reaction, such as neutralisation, oxidation, or precipitation. The termination of the reaction is indicated by some end-reaction which is usually a production, destruction, or change of colour, the formation of a permanent precipitate or the cessation of the formation of a precipitate. In determining the strength of caustic soda, for example, it is coloured blue with litmus, and a dilute solution of sulphuric acid of definite strength is added gradually until the blue colour of the litmus just changes to red, thus indicating the point of neutralisation. The volume of acid required is noted; the weight of sulphuric acid which it contains, and hence the weight of soda which it will neutralise, is known, and thus the proportion of soda in the substance is determined.

In order that a reaction may serve as the basis of a volumetric process, it must be rapid, simple, and definite, and not complicated by secondary reactions. It should remain constant through considerable variations in conditions, and should not, for example, be materially affected by the degree of concentration of the solution. A final reaction should be rapid, perfectly decisive, and should not require a large excess of the reagent for its production. In many cases a third substance is employed to indicate the completion of the reaction, and is termed an *indicator*. It is an *internal indicator* if it is added to the bulk of the liquid, an *external indicator* if drops of the liquid are removed and brought in contact with it.

The execution of volumetric processes involves the possession of accurately graduated instruments of three kinds, viz. flasks, pipettes, and burettes. The flasks should be fitted with well-ground stoppers and should have somewhat long necks, the graduation being not higher than the middle of the neck, in order that there may be sufficient empty space for efficient agitation. Flasks holding respectively 1,000 c.c., 500 c.c., 250 c.c., and 100 c.c. are used. Each flask should have two graduation marks, viz. the *containing mark*, indicating the point to which the flask must be filled in order that it may then contain the particular volume of liquid, and the *delivery mark* or point to which the flask must be filled in order that it may deliver the given volume of liquid when emptied by draining. A pipette is usually a cylindrical bulb terminating at each end in a tube, the lower



of which is drawn out to a jet, whilst the end of the upper tube is slightly contracted so that it may be readily closed by the forefinger and the flow of liquid regulated or stopped altogether. Usually a pipette has only a *delivery* mark, but occasionally they are graduated throughout their whole length and then take the form of a somewhat wide tube contracted to a jet at the bottom and terminating in a narrower tube at the top. Pipettes of 100 c.c., 50 c.c., 25 c.c., 10 c.c., and 5 c.c. capacity are most generally useful. A burette is a long tube of uniform bore, 12 to 15 mm. in diameter, graduated in cubic centimetres and tenths or fifths. A convenient capacity is 50 c.c. The older forms of instrument devised by Gay Lussac, Geissler, Binks, &c., are now little used, the convenient form described by Mohr being generally adopted. This is open at the top and contracted at the lower end, to which a glass jet is attached by means of a piece of narrow indiarubber tubing. This tubing is nipped by a spring pinchcock, which is opened by the pressure of the fingers, the flow of liquid being thus regulated. A better plan is to insert in the indiarubber tubing a short piece of glass rod the diameter of which is just sufficient to prevent the flow of liquid when the tubing remains circular. If, however, the tubing is squeezed out laterally by the pressure of the thumb and fore-

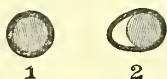


FIG. 14.

finger (fig. 14), a channel is made through which the liquid can pass, and by increasing or reducing the pressure, the flow of liquid can be regulated to a nicety. Certain of the reagents act upon indiarubber, and for these a burette with a glass stopcock should be used. This form is, in fact, the most convenient for all purposes. The stopcock may be prevented from sticking by a little vaseline or paraffin, and from slipping out by a small indiarubber ring passed over the tap and round the burette tube. Sometimes the tube carrying the stopcock is not in the same line with the burette, but is bent at right angles. This form is useful when titrating hot liquids, since the risk of heating the burette and its contents is reduced. After long use, especially with potassium bichromate and certain other solutions, the glass becomes repellent and the solution collects in drops instead of flowing down freely. This is remedied by rinsing out the burette with a small quantity of *very dilute* hydrofluoric acid.

When a burette is in use, it is important that it should be supported in a vertical position. This can be done by means of a clamp attached to a stand similar to a retort stand. Mohr recommends to slip over the top of the burette a large perforated cork which fits so tightly that it will safely carry the burette full of liquid, and yet has so much freedom of motion that the height of the burette can be readily adjusted. The burette is passed through a hole in the wooden arm of a tall stand similar to a funnel stand and the burette is supported by the cork. The hole in the wooden arm is cut through at

one side in order that the burette may be taken out without removing the cork. This hole is closed by a brass catch when the burette is in position. Several burettes may be supported by the same arm. When several different solutions are being used continually, it is convenient to have the series of burettes attached to a revolving stand so that each may be brought round to the front when required. Short test tubes inverted over the tops of the burettes serve to keep out dust.

*Standard solutions* should be kept in well-stopped bottles in a cool place protected from bright light. When several determinations of the same kind have to be made, it is convenient to keep the reservoir of standard solution attached to the burette to facilitate the filling of the latter. A glass T piece is introduced between the graduated part of the burette and the stopcock or pinchcock, and is attached by means of an indiarubber tube to a tubulus at the bottom of the bottle which contains the standard solution and stands on a shelf above the burette. If this bottle has no tubulus a glass tube bent twice at right angles, with one limb reaching to the bottom of the bottle and the other connected with the burette, is fitted into the neck of the bottle by means of a cork and is kept always full so that it acts as a siphon. There must of course be an entrance for air as the liquid flows from the bottle. The flow of liquid into the burette is regulated by a pinchcock on the indiarubber tube. If the standard solution acts upon indiarubber, all these connections must be constructed of glass tubing. Filling the burette from the bottom avoids the formation of air bubbles, but it can also be filled from the top if the tube from the stock bottle is bent slightly so that the liquid flows down the side of the burette. When the standard solution alters if exposed to air the surface of the liquid may be covered with a layer of rectified paraffin of moderately high boiling-point, or the neck of the bottle may be provided with a cork carrying a tube containing potash, or potash and pyrogallol, through which all air entering the bottle has to pass. A still better plan is to fill the upper part of the stock bottle with carbonic anhydride, or, if the nature of the solution permits, with coal gas, and connect it by means of a cork and tube with a self-acting carbonic anhydride apparatus or the ordinary gas supply. When solution is withdrawn, carbonic anhydride or coal-gas enters. By means of T tubes one carbonic anhydride apparatus or gas-tap may be made to serve several stock bottles.

*Graduation of the instruments.*—Accurate graduation of the measuring vessels is of course essential if correct results are to be obtained. In all cases the litre constitutes the starting point. Since, however, the volume of a given weight of water depends on the temperature, and since, also, the volume of the glass varies, though not greatly, with changes of temperature, it is evident that the volume of a flask will only be strictly correct at the particular temperature at which the graduation was made. Mohr proposes the adoption of 17.5°C. as the standard temperature for the graduation of instruments and the preparation of standard solutions. It is, however, better to graduate the vessels so that



they have strictly their nominal capacity at the temperature at which the graduation is made, and then the variations from the true volume will only be those resulting from the expansion of the glass, which is so small for the intervals of temperature through which the laboratory is likely to vary that it may be neglected. Whichever plan is adopted it is essential that all the instruments be graduated on the same basis, so that the ratios between them may be correct.

It is never advisable to trust the manufacturer's graduation, and the instruments should always be checked before being taken into use. A quantity of distilled water is placed in the balance room, and allowed to remain until the temperature becomes constant. The litre flask is made clean and dry, a narrow slip of paper is attached vertically to the neck near the mark, and the flask is placed on one pan of a balance capable of turning with at least 0.05 gm., and counterpoised. Weights corresponding with the weight of water which at the temperature indicated by the thermometer will occupy 1,000 c.c., are then placed in the pan; the flask is filled nearly to the mark with water, and water is gradually dropped in until the flask and weights are in equilibrium. Care should be taken that no large drops of water adhere to the inside of the neck of the flask; they can be removed by a roll of filter paper. A mark is now made on the strip of paper at the point corresponding with the lower surface of the meniscus, and the determination may be repeated. When weighing large objects of this kind the correction for the difference between the weight of the air displaced by the object and that displaced by the weights is too large to be negligible, and in the following table, taken from WARTS' DICTIONARY OF CHEMISTRY, this correction is combined with the correction for temperature:—

$t^{\circ}$	1	2	3	4	5	6	7	8	9
$x$	1.25	1.20	1.15	1.13	1.12	1.12	1.14	1.16	1.21
$t^{\circ}$	10	11	12	13	14	15	16	17	18
$x$	1.27	1.34	1.43	1.52	1.63	1.76	1.89	2.04	2.20
$t^{\circ}$	19	20	21	22	23	24	25	26	27
$x$	2.37	2.55	2.74	2.95	3.17	3.39	3.63	3.88	4.13

$x$  is the quantity to be subtracted from 1,000 to obtain the weight of 1,000 c.c. of water at the temperature  $t$ . For example, at  $18^{\circ}$  the weight of 1,000 c.c. is  $1000 - 2.20 = 997.8$  grams.

The flask which has been graduated to contain must now be graduated to deliver. The full flask is carefully emptied, and allowed to drain for a definite time—say twenty or thirty seconds—again counterpoised with the water adhering to the inside, and again filled with 1,000 c.c. of water in the manner already described. The second mark will of course be higher in the neck than the first. The other flasks are graduated in the same way, subtracting only  $\frac{1}{2}x$  from 500 grams in the case of the 500 c.c. flask,  $\frac{1}{4}x$  from 250 grams, and so on.

In order to graduate pipettes they are suspended from one arm of the balance by means of a clip, so that they hang perpendicularly and pass through a hole in the bottom of the balance case or of a specially constructed table. A convenient form of clip consists of a frame made of stout brass wire, carrying two vertical clips of sheet brass closed by sliding

collars. The upper end of the pipette is passed through the lower clip and connected by caoutchouc tubing with a glass stopcock fixed

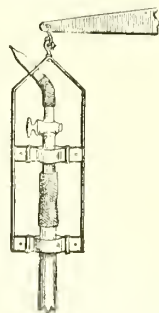


Fig. 15.

in the upper clip. The other end of the stopcock is provided with a piece of caoutchouc tubing, to which a piece of thermometer tube or a piece of wider glass tube can be attached.

The quantity of liquid which a pipette will deliver depends to some extent on the way in which it is emptied. A small quantity of liquid always remains in the tube, and this should not be blown out. The best plan is to allow the pipette to empty itself whilst held vertically, and then just touch the surface of the liquid with the lower end of the pipette. This is known as 'free flow and touch.'

A pipette is attached to the clip, and the wider glass tube which serves as a mouthpiece is attached to the stopcock, and the pipette is filled with water to a short distance above the mark and then emptied. It is now counterpoised on the balance with the adhering water inside, the wide tube attached to the stopcock being replaced by the thermometer tube, and the weights corresponding with the particular volume of water are placed in the pan. The pipette is again filled to a short distance above the mark; the thermometer tube, which is drawn out at one end, is replaced and the stopcock is opened. The water drops very slowly from the end of the pipette, and can be arrested at the moment when the balance is in equilibrium. The level of the liquid is marked on the paper gummed to the pipette.

When the instruments have been checked in this way the glass surrounding the marks is evenly coated with melted wax, through which the marks on the paper are easily seen, and the coating is scratched through by means of a needle. The mark is then covered with a small piece of filter paper, which is moistened with hydrofluoric acid, care being taken to remove air bubbles, and allowed to remain for a few minutes according to the strength of the acid. The acid is then washed off and the wax removed, and the new mark is found to be etched into the glass.

The burette is filled with distilled water at a known temperature, and 10 c.c. is run into a small weighed beaker, weighed, and this process repeated for each 10 c.c. If the graduation is not accurate a correction must be made—for example, if 10 c.c. weighs only 9.95 grams when

it should weigh 9.99, then each nominal cubic centimetre is  $\frac{9.95}{9.99} = 0.996$  of a true cubic centimetre.

*Standard solutions.*—These form the basis of all volumetric work, and great care should be exercised in their preparation. When a solution is used only for the estimation of one substance it may be convenient to adjust its strength so that each c.c. is equivalent to some simple and definite quantity of the substance, say 0.01 gram, but for general purposes the so-called *normal solutions* should be employed. A *normal solution* contains in 1,000 c.c. the equivalent in grams of the active substance. A solution of one-tenth this strength is termed a *decinormal solution*, and one of a hundredth a *centinormal solution*. A normal solution of hydrochloric acid contains 36.37 grams of real acid per litre, of sulphuric acid, 49 grams. A decinormal solution of iodine contains 12.65 grams of iodine per litre, and each litre of a decinormal solution of potassium permanganate contains 0.8 grams of active oxygen.

Standard solutions are made by weighing out a definite quantity of the pure substance, or, if the reagent is not quite pure, by weighing out an approximate quantity and titrating the resulting solution against some pure compound. In the first case exactly the required quantity may be weighed out, dissolved, and diluted to the litre, or a slightly greater quantity may be taken, accurately weighed, dissolved, and diluted to the required volume. For example, if instead of 16.96 grams of silver nitrate we weighed out 17.20 grams, then the volume of water required to make a strictly decinormal solution would be  $16.96 : 17.20 :: 1000 = 1014$ . When a solution of approximate strength is made and titrated it may be diluted to normal strength in the way just indicated. If, for example, 1 c.c. of sodium thiosulphate solution is found to be equivalent to 0.0129 gram of iodine instead of 0.01265, then  $0.01265 : 0.01290 :: 1000 : 1019.8$ , or each litre of the solution must be diluted with 19.8 c.c. of water. Accurate adjustment in this manner is difficult, and in most cases it is better to determine a *factor* by which the readings must be multiplied in order to correct for the difference between the real strength of the solution and the normal strength; thus  $\frac{\text{actual strength}}{\text{normal strength}} = \text{factor}$ .

In the case quoted  $\frac{0.01290}{0.01265} = 1.020$ , and hence 1 c.c. of the thiosulphate solution is equal to  $0.01265 \times 1.020$  grams iodine, or  $0.003537 \times 1.020$  gram of chlorine, or  $0.0043 \times 1.020$  gram of manganese dioxide, or in general terms for a normal solution,  $1 \text{ c.c.} = \frac{\text{gram-equivalent}}{1,000} \times \text{factor}$ . For a decinormal solution the denominator is of course 10,000.

*Measurements.*—In measuring out solutions &c., the vessels must be perfectly dry, which is inconvenient, or must be well drained and then rinsed out with a small quantity of the solution to be measured, which is allowed to run away.

To read correctly the level of the liquid in a burette or pipette requires certain precautions. In the first place the instrument must be held in a vertical position. Ordinary liquids form a

concave surface or meniscus, and the reading should always be taken from the lowest point of this curve, except in the case of very dark coloured solutions, when the upper line of the surface must be taken. The meniscus must be properly illuminated, and the eye at the same level, in order to avoid parallax. Mohr recommends the use of a piece of card, one half of the surface of which is black and the other white. This is attached to the burette by an indiarubber ring, and is adjusted so that the horizontal edge of the black half, which is lowest, is 2 to 3 mm., but not more, below the meniscus. The lower edge of the curve then appears black against the white background. If the card is too low the reading will be slightly too high. Illumination may also be obtained by holding a piece of white paper at an angle of about  $45^\circ$  a short distance below and behind the meniscus. A

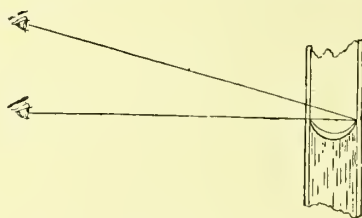


FIG. 16.

simple method of avoiding parallax is to raise the eye until the rear edge of the surface of the liquid is visible, and then lower it until the rear is just hidden by the front edge (fig. 16). The eye is now on a level with the meniscus.

Since the various solutions expand when their temperature rises, it is evident that in addition to the errors incident to all analytical processes, we have the errors due to variations in temperature. If, for instance, a standard solution has been prepared at  $10^\circ$ , 1 c.c. at  $18^\circ$  will contain less than the nominal amount of reagent. The errors due to variations within the ordinary range of temperature are so small that they may usually be neglected, and they can be minimised by keeping the temperature of the laboratory as constant as possible. The co-efficients of expansion of certain standard solutions have been determined by A. Schulze (Fr. 21, 167).

Errors due to changes of temperature may be eliminated by weighing the solutions instead of measuring. The liquid is contained in a light glass bottle, with a long jet-like neck, and a tubulus at the shoulder which can be closed by the finger and the flow of liquid thus regulated. The bottle is weighed, the solution poured gradually from it until the reaction is complete, and the bottle again weighed. The difference between the two weighings gives the quantity of solution used.

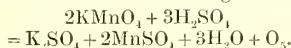
Volumetric methods may be broadly classified as I. Methods of Saturation; II. Methods of Oxidation and Reduction; III. Methods of Precipitation.

#### I. METHODS OF SATURATION v. ACIDIMETRY.

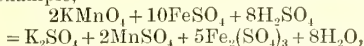
## II. METHODS OF OXIDATION AND REDUCTION.

*Potassium permanganate.*

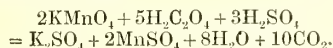
When a solution of potassium permanganate, acidified with sulphuric acid, is brought in contact with some readily oxidisable substance, it decomposes in accordance with the general equation



In the case of a solution of ferrous sulphate, for example,



and with oxalic acid



The utility of the permanganate depends upon its oxidising power, and the reaction is complete when the liquid acquires a faint permanent pink tinge, due to excess of permanganate. Usually oxidation takes place rapidly at the ordinary temperature, but solutions of oxalic acid must be heated to 60°–80°. The presence of a considerable excess of free sulphuric acid is essential. If this acid is deficient the solution becomes turbid owing to the separation of manganese oxide, the oxidation is incomplete, and the determination is spoilt. In warm solutions hydrochloric acid is decomposed with liberation of chlorine, but in cold and dilute solutions this acid is without injurious effect. It is, however, advantageous to add a certain quantity of a solution of manganese sulphate.

Permanganate solution is employed in four ways—(a) directly; (b) indirectly in the case of oxidising compounds, which are allowed to act on a definite quantity of a standard solution of ferrous sulphate, the ferrous salt remaining unoxidised being afterwards determined; (c) indirectly in the case of reducing substances, which are allowed to act on an excess of a ferric salt, the quantity of ferrous salt formed being estimated, and (d) indirectly for the estimation of metals by the determination of the amount of oxalic acid in insoluble oxalates.

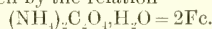
*Preparation and titration of the solution.*—The crystallised salt is dissolved in distilled water in the proportion of 5 grams per litre. This gives a solution of convenient strength, which, however, is empirical and not decinormal. It is carefully titrated by means of metallic iron or oxalic acid, and the factor with respect to the oxygen or iron equivalent may be calculated.

*Titration by metallic iron.*—About 1 gram of perfectly rust-free iron wire, preferably of the form known as 'flower' wire,<sup>1</sup> is accurately weighed into a 250 c.c. flask and dissolved in dilute sulphuric acid by the aid of heat. The flask is fitted with a cork which carries a tube bent twice at right angles, the end of the tube dipping into some hot recently boiled water in a beaker or flask. The tube is not continuous, but the two parts are joined by a piece of caoutchouc tubing which can be closed by a pinch-cock. The air is expelled from the flask by adding a small quantity of sodium carbonate,

<sup>1</sup> Piano wire may be used, but it contains on an average only 99·6 per cent. of iron, and hence the weight taken must be multiplied by 0·996 to obtain the true weight of the iron.

and the hydrogen evolved during solution bubbles through the hot water. When all the iron is dissolved the solution is boiled to expel the hydrogen from the flask. It is then allowed to cool, and as the steam condenses the hot water is driven into the flask by the pressure of the atmosphere. When it reaches the mark the pinch-cock is closed. The flask is now allowed to become quite cold, and is filled up to the mark and the contents thoroughly mixed by agitation; 50 c.c. is withdrawn, mixed with dilute sulphuric acid, and permanganate added gradually from a burette until the liquid acquires a faint permanent pink colour. This operation is repeated. The number of cubic centimetres required gives the value of the permanganate in terms of iron, and from the relation  $2\text{FeO} + \text{O} = \text{Fe}_2\text{O}_3$ , or  $2\text{Fe} = \text{O}$ , its oxygen value is readily calculated.

*Titration by oxalic acid.*—The acid itself is not easily obtained of perfectly definite composition, and the ammonium salt  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (mol. wt. 142) should be used. About 1 gram of the salt is dissolved in 250 c.c. of water, 50 c.c. of this solution is withdrawn, mixed with dilute sulphuric acid in somewhat large quantity, heated to 60°–80°, and permanganate added gradually until a permanent pink colouration is obtained. The vessel is again placed on the sand-bath and heated up to 60°–80°, and if the pink colour remains oxidation is complete; if it disappears a further quantity of permanganate is added until the colouration is permanent. From the relation  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} = \text{O}$ , the oxygen value of the permanganate is readily calculated. If the solution is to be used mainly for the estimation of iron the value in terms of this metal is given by the relation



For general purposes it is convenient to express the strength of the solution in terms of available oxygen; thus 1 c.c. = 0·0080 × factor.

**Bismuth.** The solution, free from hydrochloric acid, is mixed with a considerable excess of oxalic acid, the precipitate filtered off, and boiled repeatedly with hot water to convert it into basic oxalate  $\text{Bi}_2(\text{C}_2\text{O}_3)_3 \cdot \text{O}$ , which is treated in the same way as calcium oxalate;  $\text{O} = \text{Bi}$ .

**Cadmium.** The neutral solution is mixed with excess of oxalic acid and a large volume of alcohol. The crystalline cadmium oxalate is washed with dilute alcohol, dried at 100°–110° until all alcohol is expelled, and then treated in the same way as calcium oxalate (v. also *Hydrogen sulphide*).

**Calcium** is precipitated from a hot slightly alkaline solution by excess of ammonium oxalate, and the precipitate is thoroughly washed with hot water. It is then decomposed by treatment with excess of hot dilute sulphuric acid, the solution diluted to a definite volume, and the oxalic acid estimated in an aliquot part by means of permanganate;  $\text{O} = \text{H}_2\text{C}_2\text{O}_4 = \text{Ca}$ .

The calcium solution may be mixed with a measured excess of a standard solution of ammonium oxalate; diluted to a definite volume, and when the precipitate has settled, an aliquot part of the clear liquid may be withdrawn and the excess of oxalate determined, or the liquid may be filtered and the excess of oxalate determined in the filtrate.



**Ferrocyanides.** The dilute solution of an alkaline ferrocyanide is mixed with a considerable quantity of sulphuric acid, and permanganate added gradually until the pure yellow solution acquires a distinct orange tinge. If difficulty is experienced in seeing the end reaction, a drop of the solution may be brought in contact with a drop of a dilute ferric chloride solution on a white plate. So long as any ferrocyanide is unaltered a blue precipitate is formed, but when all the ferrocyanide is oxidised only a brownish colouration is obtained;  $O = 2K_2FeC_6$ . Insoluble ferrocyanides are decomposed by potash or soda solution, and the ferrocyanide determined in the filtrate after acidification. A solution of permanganate containing not more than 1 gram of the salt per litre should be used, and it should be standardised by means of pure potassium ferrocyanide.

**Ferricyanides** in solution are made strongly alkaline with potash or soda, heated to boiling, and ferrous sulphate solution added gradually until the precipitate just becomes black. The ferrous hydroxide reduces the ferricyanide to ferrocyanide. The liquid is filtered, the precipitate thoroughly washed with hot water, and the ferrocyanide estimated in the filtrate;  $O = 2K_3FeC_6$ . Insoluble ferricyanides are first decomposed by potash or soda.

**Hydrogen sulphide.** The solution is added to an excess of an acidified solution of ferric sulphate free from any ferrous salt, and allowed to remain for about an hour in a well-closed vessel. The ferric sulphate is reduced to the ferrous salt. The liquid is diluted with cold but recently boiled water until nearly colourless, and titrated with permanganate;  $O = H_2S$ .

This method may be applied to the indirect estimation of metals, such as cadmium or zinc, the sulphides of which are soluble in an acid solution of ferric sulphate. The metals are precipitated as sulphides, and the well-washed precipitates are dissolved in an excess of acidified ferric sulphate solution, and the amount of ferrous sulphate formed is estimated  $O = H_2S = Zn = Cd$ . Alkaline sulphides are precipitated in the form of zinc sulphide.

**Iron** in the form of ferrous salts is estimated as described in the method of determining the strength of the permanganate, and this method is available for the determination of ferrous salts in presence of ferric salts. To estimate the total iron the ferric salts are reduced by means of zinc or some other reducing agent (*v. IRON*).

**Lead** is precipitated as oxalate by oxalic acid (not ammonium oxalate) in the absence, as far as possible, of alkaline salts, and especially of ammonium salts, and the lead oxalate is treated as in the case of calcium;  $O = Pb$ .

**Manganese** in the form of manganese dioxide is estimated by dissolving in a measured excess of a strongly acid solution of ferrous sulphate and determining the proportion of the salt left unoxidised, or by dissolving it in an acid solution of a known quantity of oxalic acid or sodium oxalate, and determining the residual oxalic acid;  $O = MnO_2$ .

Pattinson (C. J. 1879, 365) precipitates the manganese as dioxide in presence of a ferric salt by adding calcium carbonate after treatment

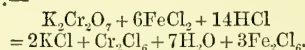
with bleaching powder solution or bromine, and dissolves the precipitated dioxide in excess of a strongly acid standard solution of ferrous sulphate, which is re-treated with permanganate or bichromate. If the amount of iron present in the original solution is equal to that of the manganese, the latter is entirely converted into the dioxide, the formation of lower oxides being prevented. Zinc sulphate has a similar effect (Kessler).

**Oxalic acid**, free or in combination, is estimated in the manner adopted for determining the strength of the permanganate;  $O = H_2C_2O_4$ .

**Zinc** is estimated as oxalate in the same way as cadmium (*v. Cadmium*), or by precipitation as sulphide (*v. Hydrogen sulphide*).

#### *Potassium bichromate.*

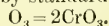
This reagent may be employed in place of permanganate for the estimation of iron, and has the advantage that it can be used in presence of hydrochloric acid with equally good results. An excess of free acid is essential. The reaction in the case of ferrous chloride is as follows:—



A decinormal solution is obtained by dissolving 4.907 grams of the dry recrystallised salt in 1,000 c.c. of water. The solution may be standardised against metallic iron in the same way as permanganate. The green colour of the chromic salt, however, prevents the excess of bichromate from being seen, and hence an external indicator is necessary. Drops of a dilute solution of potassium ferricyanide, free from ferrocyanide, are placed on a white plate, and drops of the iron solution are removed from time to time with a glass rod and brought in contact with a drop of the ferricyanide. So long as any ferrous salt is unoxidised a blue precipitate is formed, but when all the iron is in the ferric state only a brown colouration is obtained. The approach of the end is indicated by the decrease in the intensity of the blue colour, and a little time should be allowed for the action of the bichromate towards the close of the reaction. The ferricyanide solution should be put on the plate just before it is wanted, and only a few drops at a time, since when exposed to air and light it is partly converted into ferrocyanide.

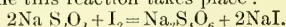
Potassium bichromate can not only be used for the estimation of iron, but also for indirect determination in which an oxidising agent acts upon a known quantity of a ferrous salt or a reducing agent acts upon an excess of a ferric salt.

**Chromic acid and chromates** can be estimated by adding a known quantity to a measured excess of an acid solution of ferrous sulphate of definite strength, the excess of ferrous sulphate being determined by standard bichromate;



#### *Iodine and sodium thiosulphate solutions.*

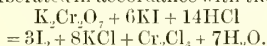
These two solutions, of decinormal strength, are used in conjunction with one another. When sodium thiosulphate is brought in contact with free iodine this reaction takes place:



The termination of the reaction is indicated by

the disappearance of the yellow colour, or a small quantity of starch paste may be added to the solution. So long as any free iodine is present the liquid is dark blue, but as soon as all the iodine is converted into sodium iodide it becomes colourless. A solution of sodium thiosulphate can be used, not only for the estimation of free iodine, but also of any substance that directly or indirectly liberates a definite quantity of iodine from potassium iodide. Iodine solution is employed mainly as an oxidising agent.

**Sodium thiosulphate solution.** 24.8 grams of the recrystallised salt  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  per litre. The solution remains unaltered for a long time if kept in a cool place in the dark. Its strength is readily determined by dissolving about 1 gram of potassium bichromate in 250 c.c. of water, and adding 25 c.c. of this solution to 200 c.c. of water containing about 2 grams of potassium iodide and 5 c.c. of strong hydrochloric acid. Iodine is liberated in accordance with the equation

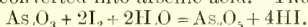


Sodium thiosulphate is added to the liquid until most of the iodine has disappeared. A small quantity of starch paste is put in, and the addition of the thiosulphate is continued until the blue colour is just discharged. The iodine value of the thiosulphate is calculated from the weight of bichromate taken. If a decinormal solution of bichromate is at hand it may of course be used.

**Iodine solution.** 12.65 grams of dry resublimed iodine is agitated with 250 c.c. of water and 20 grams of potassium iodide free from iodate until the iodine is completely dissolved, and the solution is diluted to 1,000 c.c. If necessary it may be standardised by means of the thiosulphate solution which has itself been standardised in the way described.

**Starch paste** is made by rubbing pure starch into a cream with water, pouring this cream into about 150 parts of boiling water, and boiling for a short time.

**Arsenious acid** in contact with iodine solution is converted into arsenic acid. Thus



Sodium hydrogen carbonate, free from normal carbonate, is added to neutralise the hydriodic acid, and the solution is titrated with standard iodine, using starch as an indicator, until the blue colour is persistent for at least three minutes. A reddish tint is apparent before the reaction is finished, and the final blue colouration disappears after standing for some time.  $\text{I}_2 = \text{As}$ .

**Arsenic acid** is determined by first estimating any arsenious oxide in one portion of the solution, then heating another portion with sulphurous acid to reduce the arsenic acid to arsenious acid, boiling to expel all sulphurous anhydride, and titrating with iodine when cold. The increase in the quantity of iodine required gives the amount of arsenic acid.

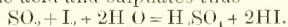
**Antimony** in tartar emetic and antimonious compounds generally is estimated in a precisely similar manner.  $\text{I}_2 = \text{Sb}$ .

**Hydrogen sulphide.** When iodine is brought in contact with a solution of hydrogen sulphide the following reaction takes place:  $\text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S}$ . In concentrated solutions, however, the reaction becomes complicated and the liquid

titrated must not contain more than 0.04 per cent. of the gas. A measured quantity of the solution is mixed with starch paste and the iodine solution added until a permanent blue colouration is produced. A measured quantity of iodine solution, 5 to 10 c.c. in excess of the volume indicated by this preliminary experiment, is placed in a beaker, largely diluted with water, the same volume of hydrogen sulphide solution run in as was taken in the first case, and the excess of iodine determined by means of thiosulphate. This plan removes errors due to exposure to air &c., and a slightly higher quantity of iodine solution will be required than in the preliminary experiment.

**Hydrocyanic acid and cyanides.** The solution is made slightly alkaline, if necessary, with soda or potash, then mixed with excess of water saturated with carbonic anhydride, and titrated with iodine solution, the termination of the reaction being indicated either by the pale yellow colour of the liquid or by starch. The reaction is  $\text{KC}y + \text{I}_2 = \text{KI} + \text{C}y\text{I}$ , i.e.  $\text{I}_2 = \text{C}y$ .

**Sulphurous acid and sulphites.** Iodine solution oxidises sulphurous acid and sulphites to sulphuric acid and sulphates thus—



In the case of the free acid, however, the reaction becomes complicated, especially in concentrated solutions, and a condition of equilibrium is established between the above reaction and  $\text{SO}_2 + 4\text{HI} = \text{S} + 2\text{H}_2\text{O} + 4\text{I}$  (Volhard, A. 242, 93). The error due to this cause is avoided by adding the sulphurous acid solution gradually to the iodine, but it is not advisable that the solution should contain more than 1 p.c. of the gas. A measured excess of iodine solution is placed in a beaker or flask, the sulphurous acid solution added, and the excess of iodine determined by means of sodium thiosulphate. Solid sulphites are weighed out, dissolved in excess of standard iodine solution, and the remaining iodine estimated by thiosulphate (*v.* Giles and Scheerer, S. C. I. 3, 197 and 4, 303).

**Thiosulphates** are estimated directly by titration with iodine.

**Tin** in solution in the form of a stannous salt is mixed with excess of sodium potassium tartrate and excess of sodium hydrogen carbonate, and titrated with standard iodine, using starch as an indicator;  $\text{I}_2 = \text{Sn}$ .

#### *Estimations by thiosulphate.*

**Bromine and chlorine** in the free state are estimated by adding a measured volume of the solution to an excess of a solution of potassium iodide and titrating with thiosulphate.  $\text{I} = \text{Cl} = \text{Br}$ .

**Peroxides, chromates, chlorates, iodates**, and all substances which liberate a definite quantity of chlorine when treated with hydrochloric acid, can be estimated by sodium thiosulphate, the chlorine being absorbed in potassium iodide solution, and the liberated iodine determined by titration. The substance, together with strong hydrochloric acid, is placed in a small flask, the delivery tube from which passes into a retort or bulb U-tube containing an excess of a solution of potassium iodide. The contents of the flask are boiled rapidly for at least ten minutes, and the liberated iodine is titrated by thiosulphate. This titration

should be done at once, since hydrochloric acid distils over, and if the acidified solution of potassium iodide is exposed to the air a further quantity of iodine is slowly liberated. Manganese ores, chromates, bichromates, and chlorates

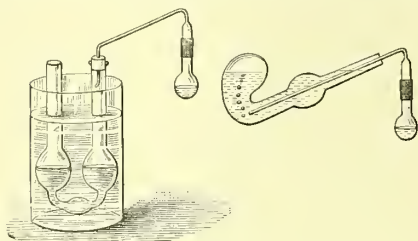


FIG. 17.

may be treated in this way. Iodates and bromates are best digested with potassium iodide and hydrochloric acid in a bottle with an accurately fitting stopper which is tightly tied down.

### III. METHODS OF PRECIPITATION.

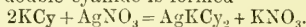
*Silver nitrate.* This is the principal reagent in this class. A decinormal solution is obtained by dissolving 16.96 grams of the pure, dry, recrystallised silver nitrate in 1,000 c.c. of water.

*Potassium chromate* is used as an indicator in the form of a saturated solution. This is mixed with silver nitrate until a small quantity of a red precipitate is formed, and after the liquid has been thoroughly agitated with this precipitate it is filtered. Any chloride present is thus removed.

When a solution of silver nitrate is added to a solution of a chloride, bromide, or iodide, which has been mixed with a small quantity of potassium chromate, the silver combines with the haloid, and any chromate that may be formed is at once decomposed. As soon, however, as the whole of the haloid has been precipitated, silver chromate is formed, and its presence imparts to the liquid a reddish tint which indicates the termination of the reaction.

*Chlorides, bromides, iodides.* The solution if alkaline is neutralised with nitric acid, if acid it is neutralised by adding precipitated calcium carbonate free from chlorides. Two or three drops of potassium chromate are added, and silver solution is run in from the burette until the pale yellow liquid suddenly acquires a reddish tint. The approach of this point is indicated by the increase in the time required for the disappearance of the silver chromate. The change is more readily seen in a yellow light, and is especially distinct in the monochromatic light from a sodium flame, the silver chromate appearing almost black. It is found that 0.1 c.c. of the decinormal silver solution is required to produce sufficient silver chromate to give an end reaction when the volume of the liquid is 100 to 150 c.c., and this is subtracted from the burette reading before calculating the amount of chlorine &c. Silver chromate is much more soluble in solutions of ammonium nitrate and certain other salts than in water, and hence in presence of these salts considerably more silver solution is required to produce the end reaction (Carpenter):  $\text{AgNO}_3 = \text{Cl} = \text{Br} = \text{I}$ .

**Hydrocyanic acid and cyanides.** When silver nitrate is added to potassium cyanide a soluble double cyanide is formed



If, however, more silver nitrate is added, the double cyanide is converted into simple silver cyanide, which is precipitated. The formation of a permanent precipitate indicates the termination of the first stage of the reaction. In the presence of chlorides no permanent precipitate appears until the cyanide has all been converted into the double cyanide.

Hydrocyanic acid is measured in a pipette to the upper part of which is attached a tube containing solid potash, and is run into sufficient soda or potash solution to neutralise it and yield a slightly alkaline solution, which is then diluted considerably. Alkaline cyanides are dissolved in the usual way. If chlorides are absent it is advisable to add a small quantity of sodium chloride. Silver nitrate is then added gradually to the solution, with constant agitation, until a slight permanent precipitate is formed. This is best seen against a sheet of black paper. The volume of silver solution used is equivalent to half the cyanide existing in the solution—that is to say,  $\text{Ag} = 2\text{Cy}$ .

#### *Volhard's Method.*

A silver solution is used in conjunction with a solution of an alkaline thiocyanate, ferric sulphate being employed as an indicator. When solutions of a silver salt and a thiocyanate are mixed in presence of a ferric salt, so long as silver is in excess silver thiocyanate is precipitated, and any ferric thiocyanate which may form is at once decomposed. As soon, however, as the thiocyanate is in slight excess the liquid acquires a permanent faint-brown tint owing to the formation of ferric thiocyanate. This method may be applied to the estimation of silver, and also, by adopting the method of reverse titration, to the estimation of substances which are completely precipitated by silver nitrate. It has the great advantage of being applicable to acid solutions (A. 190, 47).

*Silver nitrate solution.* The ordinary decinormal solution is employed.

*Thiocyanate solution.* 8 grains of purified ammonium thiocyanate, or the corresponding quantity of the potassium salt, is dissolved in 1,000 cc. of water, and after titration the solution is diluted until it exactly corresponds with the silver solution.

*Ferric sulphate solution* is prepared by oxidising ferrous sulphate with nitric acid, boiling till all oxides of nitrogen are expelled, and diluting until the solution contains about 10 p.c. of the salt. A saturated solution of ferric alum may also be used.

*Titration.*—10 or 20 c.c. of the standard silver solution is diluted to about 200 c.c., mixed with 5 c.c. of the iron solution, and sufficient pure nitric acid to remove any colouration produced by the iron salt alone. The thiocyanate solution is then added gradually from a burette, with constant agitation until the liquid acquires a permanent pale brown colouration. The titration of other solutions is done in the same way. The liquid must be cold, and it is advisable that the volume should not differ greatly from that



taken when standardising. Not less than 5 c.c. of iron solution should be present in 200 c.c., and nitric acid free from nitrogen oxides must be added in sufficient quantity to remove any coloration due to the iron.

**Silver** is determined by direct titration in presence of a moderate quantity of free nitric acid. Mercury and palladium must be absent, but other metals usually associated with silver have no injurious effect. If, however, the proportion of copper present exceeds 70 p.c. it must be reduced by adding a known quantity of silver.

**Chlorides, Bromides, and Iodides.** The solution is acidified with nitric acid, mixed with a measured excess of standard silver solution, and the excess of silver determined by means of the thiocyanate solution. Silver chloride is decomposed by alkaline thiocyanates, and hence it is advisable to filter off the precipitate before titrating; but this is not necessary in the case of bromides or iodides.

#### COLORIMETRIC METHODS.

These methods are especially valuable for the estimation of very small quantities of substances, and are capable of giving very accurate results. The depth of tint produced by some characteristic colour reagent in a given volume of the solution is compared with the tint produced by the same reagent in an equal volume of a solution containing a known quantity of the substance to be determined. The tint in the comparison tube can be varied by varying the proportion of the substance which it contains, and when the tints are equal the quantities of the substance in each tube are also equal. The quantity in one tube is known, and hence that in the other is determined. It is important that the comparison be made under comparable conditions with respect to degree of acidity or alkalinity, proportion of the reagent and the like. It is also important that the depth of tint should not be materially affected by the presence of other saline substances in the solution under examination.

The following substances may be determined by these methods:—

**Lead**, with hydrogen sulphide.

**Copper**, with hydrogen sulphide or potassium ferrocyanide (Carnelley, C. N. 32, 308).

**Iron**, with potassium ferrocyanide (Carnelley, C. N. 30, 257).

**Iron**, with potassium thiocyanate (Thomson, C. J. 1885, 493).

**Ammonia**, by Nessler's solution (*v. WATER*).

**Iodine**, in solution in carbon bisulphide, or with starch.

The principle may likewise be applied to the comparison of dye-stuffs, provided that the solutions are sufficiently diluted (*v. COLORIMETER*).

#### INDIRECT METHODS OF DETERMINATION.

In some cases the separation of two substances is either impossible or inconvenient, but we can calculate their relative proportions if we are able to obtain as many independent relations as there are substances to be determined. If, for example, we have a mixture of sodium and potassium in the form of chlorides, and we determine the weight of that mixture and the weight of chlorine which it contains, the rela-

tive proportions of sodium and potassium can be calculated. Let  $A$  be the weight of the mixed chlorides, and  $B$  the weight of chlorine which they contain; then  $A - B = C$ , the joint weight of the sodium and potassium. Let  $x$  = the amount of potassium, and  $y$  the amount of sodium actually present; then

$$x + y = C$$

$$\frac{\text{Cl}}{\text{K}}x + \frac{\text{Cl}}{\text{Na}}y = B,$$

and from these two equations  $x$  and  $y$  are readily calculated. The symbols of the elements are used with a quantitative significance.  $\frac{\text{Cl}}{\text{K}}$  is the

amount of chlorine which combines with 1 part of potassium,  $\frac{\text{Cl}}{\text{K}}x$  is the amount of chlor-

ine combined with  $x$  parts of potassium, and similarly in the case of sodium. The general form of the equation is the same for every case of two metals combined with one acid radicle, or two acid radicles combined with one metal.

Take as an example of a different kind, the estimation of bromine by passing chlorine over a weighed mixture of silver bromide and chloride. The loss of weight due to the displacement of Br (79.75) by Cl (35.37) is proportional to the amount of bromine present. Let  $w$  represent the loss of weight, then  $\text{Br} - \text{Cl} = w$ . Now  $\text{Cl} = \frac{35.37}{79.75}$  and hence  $\text{Br} - \frac{35.37}{79.75}\text{Br} = w$ , or  $\text{Br} = \frac{1.797w}{1.797w}$ . The loss of weight multiplied by 1.797 gives the quantity of bromine present.

Indirect methods only give useful results when the atomic or molecular weights of the two substances differ considerably, and when the quantities present are approximately equal. The results are affected to a considerable extent by comparatively small experimental errors.

#### ANALYSIS OF CARBON COMPOUNDS.

The majority of carbon compounds contain carbon, hydrogen, and oxygen, or carbon, hydrogen, oxygen, and nitrogen; a smaller number contain one or more of the haloid elements, or sulphur; a still smaller number phosphorus, arsenic, or silicon. There are also the metallic salts of the various acids, and other metallic derivatives.

##### Qualitative Examination.

**Carbon** is converted into carbon dioxide when the substance is heated with cupric oxide.

**Hydrogen.** The substance is heated to a temperature below that at which decomposition begins, until all water existing as such is expelled, and is then heated with finely divided and recently ignited cupric oxide; the hydrogen is evolved as water.

**Nitrogen.** Many carbon compounds containing nitrogen evolve this element in the form of ammonia when heated with caustic soda or soda-lime, but this test is not applicable to nitro-, nitroso-, azo-, and diazo-derivatives.

Many nitro-, nitroso-, and diazo-derivatives evolve oxides of nitrogen, with or without explosion, when heated.

Nitrogen in all classes of carbon compounds, with the exception of the diazo-compounds, may be detected by heating the substance with

metallic sodium, together with some sodium carbonate if the substance is explosive. The nitrogen is converted into sodium cyanide, and the cooled mass is extracted with water and the cyanogen detected by the Prussian blue or thiocyanate test. Nitrogenous carbon compounds containing sulphur yield, when heated with sodium, a thiocyanate, and the Prussian-blue test cannot be used. The thiocyanate may, however, be converted into cyanide by adding finely divided iron with the sodium.

Halogens are detected by heating the substance with pure lime or pure soda-lime, extracting with water, slightly acidifying with nitric acid and testing with silver nitrate. Highly nitrogenous compounds, when heated with lime, are apt to yield calcium cyanide; hence the supposed precipitate of silver haloid should always be tested for cyanide, unless nitrogen is known to be absent. With soda-lime no cyanide is formed.

**Sulphur and phosphorus** in non-volatile substances are detected by fusing with soda or potash mixed with about one-fifth its weight of potassium nitrate, and testing the product for sulphuric or phosphoric acid. Volatile or non-volatile substances may be oxidised by heating in a sealed tube at  $150^{\circ}$  to  $300^{\circ}$ , according to circumstances, with fuming nitric acid of sp.gr. 1.5. Sulphur and phosphorus are oxidised to sulphuric and phosphoric acid respectively.

#### *Quantitative Determinations.*

##### **A. Carbon and hydrogen in absence of nitrogen, halogens, &c.**

The simplest and most convenient method for general purposes is to burn the compound in a glass tube in a current of oxygen, assisted by cupric oxide; the carbon is converted into carbon dioxide, which is absorbed by potash; the hydrogen is converted into water which is absorbed by calcium chloride.

Erlenmeyer's modification of Von Babo's furnace is generally employed. The heat is supplied by a row of 20 to 25 Bunsen burners, each of which is provided with a tap and a perforated collar for regulating the supply of air. The flames strike the under side of a semicircular fire-clay or sheet-iron trough or gutter in which the combustion tube rests on a layer of magnesia or asbestos. Inclined at an angle over this gutter on either side is a row of fire-clay tiles by which the flame is reverberated upon the upper part of the glass tube, which is thus heated all round. Each tile can be pulled back and rested against an iron rail which runs down each side of the furnace, and thus any part of the tube can be readily examined, and moreover the tiles can be made to assist in regulating the temperature.

In Hofmann's furnace (A. 107, 39) the tube is heated by two double rows of perforated cylindrical fire-clay burners placed over ordinary fish-tail burners. The tube rests upon the top of a central row of much shorter burners. The burners are inclosed by flat vertical tiles and flat tiles are laid horizontally on the top.

In the Glaser (A. Suppl. 7, 213) furnace the heat is provided by a row of Bunsen burners. The tube is supported by a series of semicircular perforated iron plates, placed close

together. The flames strike the bottom of these plates and then pass through the perforations and strike against the fire-clay covers, by which they are reverberated on the tube, so that the latter is heated from the top and sides as well as from the bottom. The tube is usually wrapped round with wire gauze. This furnace will give higher temperatures than the Erlenmeyer furnace, but consumes more gas.

The combustion tube should consist of infusible potash or Bohemian glass 1.5 to 2 mm. thick, with an internal diameter of 12-15 mm. It should be of such a length that it projects about 2 cm. from each end of the gutter. Pieces of copper wire gauze about 2 cm. broad, heated in a flame to remove grease, are rolled up into plugs which fit moderately tightly in the tube, and one of these plugs is pushed into the tube to a distance of about 25 cm. from one end. The tube is then filled with freshly ignited granular cupric oxide to within 5 or 6 cm. of the other end, and a second plug is inserted. The granules of cupric oxide should be fairly regular in size, and 1.5 to 2 mm. cube. Another plug about 10 cm. long is made by rolling a piece of copper gauze round a stout copper wire 12 cm. long, and bending the projecting end of the latter into a loop by means of which it can be withdrawn from the tube. This plug is placed in the other end of the tube behind the boat. The end of the tube nearest to the copper oxide is fitted with a dry caoutchouc cork perforated to receive the tube of the absorption apparatus; the other end is closed by a similar cork which carries a piece of tubing of very narrow bore, which is connected with the apparatus for drying the oxygen.

The substance to be analysed is contained in a platinum boat about 70 mm. long and 8 mm. deep, of such diameter that it slides easily in the combustion tube. It may conveniently be inclosed in a small well-corked tube whilst being weighed.

The water is absorbed by granulated anhydrous calcium chloride, which is treated with a current of dry carbon dioxide and then with a current of dry air to convert any calcium oxide present into carbonate and thus prevent the

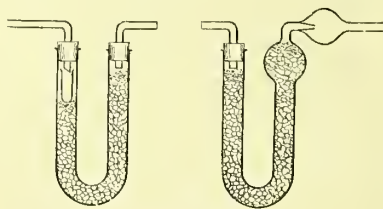


FIG. 18.

absorption of carbonic anhydride. The calcium chloride may be contained in a straight tube or a U-tube. The former consists of a tube about 13 cm. long and 12-15 mm. diameter, terminating in a bulb connected with a second smaller bulb which terminates in a short tube of about 2 mm. internal diameter fitting directly into the cork in the front end of the combustion tube. The smaller bulb is empty and serves to condense the greater part of the water, but the larger bulb and the wider tube are filled with calcium

chloride kept in its position by plugs of cotton wool.

If a U-tube is employed it should be provided with a small side bulb for condensing the water, the tube from this bulb fitting directly into the cork in the combustion tube, whilst the other limb of the U-tube is closed by a caoutchouc cork carrying a narrow tube bent at a right angle and connected with the potash bulb. In the absence of the side bulb, each limb of the tube is closed by a caoutchouc cork carrying a narrow tube bent at a right angle, one of these tubes fitting directly into the cork of the combustion tube, and the other being connected with the potash bulb. A small test tube, 2-3 cm. long, placed in the upper part of the first limb of the U-tube, collects the greater part of the water, and thus protects the calcium chloride.

A U-tube containing pumice moistened with strong sulphuric acid may also be used to collect the water, but bulbs filled with the acid must not be used, since it dissolves an appreciable quantity of carbon dioxide. Whether calcium chloride or sulphuric acid is used to absorb the water, the same substance must be used to dry the current of oxygen.

The carbon dioxide is absorbed in a strong solution of potassium hydroxide made by dis-

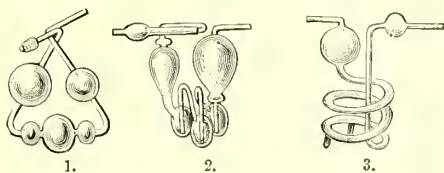


FIG. 19.

solving this substance in an equal quantity of water. The solution is contained in 'potash bulbs,' of which there are many forms. Geissler's is the most convenient, since it will stand on its own base (No. 1, fig. 19). Liebig's original form (No. 2) is still used, but the more recent form devised by Winkler (No. 3) probably secures the most efficient absorption, especially when the current of gas is somewhat rapid. The Geissler or Liebig bulbs must contain such a quantity of potash solution that it washes up to a certain extent in the last bulb, but yet is not sufficient to fill the large first bulb in case a vacuum is produced by rapid absorption of the gas. In addition to the potash bulbs, a U-tube filled with granulated soda-lime, with a layer of calcium chloride 2 cm. deep in the upper part of each limb, is used to absorb the last traces of the gas and any small quantity of moisture that may be given off from the potash solution. Two such soda-lime tubes may be used in place of potash bulbs.

The tube containing the soda-lime is connected with a U-tube filled with calcium chloride, to protect the absorption apparatus from moisture, and this is connected with a bell jar standing in a trough filled with water. The water is sucked up in the bell jar to a height of about 20 cm. above the level of the liquid in the trough, and thus the combustion is conducted under slightly reduced pressure, and the risk of any outward leakage of the gases is removed.

A screw pinchcock is placed on the caoutchouc tube connecting the bell jar with the absorption apparatus.

The oxygen is dried and purified by passing through a strong solution of potash and then through two long U-tubes containing calcium chloride. Instead of the U-tubes we may use a tall cylinder with the lower half filled with soda-lime and the upper with calcium chloride.

*The operation.*—The tube is placed in the furnace and connected at one end with the drying apparatus and at the other with the calcium chloride tube and bell jar, but not with the absorption apparatus. It is gradually heated to redness, a current of dry oxygen is passed through for half-an-hour to remove all moisture and organic matter, and the tube is allowed to cool. The solid or non-volatile liquid substance is weighed into the platinum boat, which is introduced into the tube by removing the long copper plug at the back, and the latter is then replaced. The front end of the tube is then connected with the absorption apparatus and the bell-jar, and the other end is connected with the drying tubes and the oxygen reservoir. If the apparatus is airtight the water in the bell jar should remain at the same height, and no bubbles should pass through the absorption apparatus so long as the oxygen tap is turned off. The burners under the front part of the tube are now lighted and the temperature gradually raised until the tube is at a dull red heat to within 12 cm. of the boat. The tube in contact with the cork at the front end should be so hot that it can only just be touched by the finger, and this temperature should be maintained throughout the operation by regulating the first two burners, in order to prevent condensation of moisture without decomposing the cork. If any water should condense it may be volatilised by bringing one of the hot tiles close over the tube. The last two or three burners under the long copper plug at the back are now lighted and the temperature gradually raised to dull redness, whilst at the same time the copper oxide is heated to within 5-6 cm. of the boat, and a current of oxygen is passed through the tube at the rate of a bubble every two seconds. One of the burners under the boat is then lighted and the boat very gradually heated, combustion being regulated so that the bubbles passing into the potash bulbs can easily be counted. When the substance is completely carbonised the temperature of the boat is raised and the current of oxygen increased to a bubble per second. Towards the close of the operation the boat is heated to redness and a somewhat more rapid current of gas is passed. It is not necessary to heat the tube above redness and a higher temperature produces distortion. When combustion is complete the current of oxygen is continued for a short time to drive out all carbon dioxide and reoxidise any reduced copper. When the oxygen bubbles through the potash bulbs at the same rate as through the drying apparatus, the oxygen reservoir is disconnected and a current of air is drawn through the whole apparatus to expel the oxygen. At the same time the tube is gradually cooled and is ready for a second operation. If the



tube is carefully heated and cooled it may be used for a very large number of analyses. The absorption apparatus is disconnected and weighed. All the weighings should be made without the plugs of caoutchouc tubing and glass rod which are used to protect the contents of the tubes and bulbs from the air.

Volatile liquids are inclosed in a small thin cylindrical glass bulb 3 cm. long, with a capillary neck, readily made by drawing out a piece of wider tubing. It is weighed, gently heated, and the capillary tube immersed beneath the liquid. As the tube cools a small quantity of the liquid enters. This is heated to boiling, and when the air is expelled the end of the tube is again placed in the liquid, and when the vapour condenses the bulb is completely filled. If the liquid is very volatile the capillary end may be sealed before weighing the tube, but usually this is not necessary. The bulb is placed in the boat with the capillary end open and directed towards the copper oxide. Combustion is conducted as already described, but much greater care is required, especially if the liquid is very volatile. The front part of the copper oxide must be quite red-hot before the liquid begins to volatilise, and it is advisable that the bulb be empty before the copper oxide near the boat is heated. With an iron gutter sufficient heat is conducted to vapourise volatile liquids, but in other cases a very low flame may be used or one of the hot tiles may be held over the boat. In all cases it is difficult to prevent diffusion of vapour into the back of the tube and even into the drying apparatus. The long copper plug at the back increases the speed of the current by decreasing the diameter of the passage, and the narrow diameter of the entrance tube assists in a similar manner, but in all cases of the analysis of a volatile substance a slow current of air should be passed almost from the beginning. Later, oxygen should be passed, but not too soon, otherwise an explosive mixture may be formed. The open tube in fact does not yield such satisfactory results with volatile liquids as with other substances, and in such cases combustion should be made by the following method:—

B. *Liebig's original method as modified by Bunsen.* Granular copper oxide and some of the finely divided oxide are heated strongly, and while still hot are placed in flasks with long necks which are then tightly corked. The combustion tube

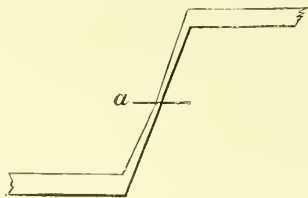


FIG. 20.

is drawn out at one end in the manner shown in the figure, and sealed at the point *a*. A layer of granular copper oxide about 10 cm. long is first introduced by placing the combustion tube into the neck of the flask containing it, and

then 2–3 cm. of the finely divided oxide. The substance (about 0.5 gram) is now introduced from a long narrow weighing tube which can be inserted into the mouth of the combustion tube, and 5–6 cm. of the finely divided oxide is added and intimately mixed with the substance by means of a long copper wire the lower end of which has two twists like a corkscrew. The wire and sides of the tube are rinsed with some of the oxide, and the tube is filled with the granular oxide to within 5–6 cm. of the top, and a plug of copper gauze inserted. Every care must be taken to prevent absorption of moisture by the copper oxide. The remainder of the operation is conducted as described above, and when combustion is complete the drawn-out end of the tube is connected with a drying apparatus, the tip broken off inside the caoutchouc tube, and a current of oxygen and afterwards of air passed through the apparatus.



FIG. 21.

In whichever way the combustion is made it is found that the percentage of hydrogen is always about 0.1–0.15 too high, a result at-

FIG. 22.

tributed to the difficulty of perfectly drying the copper oxide &c. It is frequently stated that an open tube rarely gives correct results the first time it is used; but this is solely due to neglect of the precaution of first heating in a current of oxygen (p. 147).

C. *Combustion with lead chromate.* Substances such as graphite, resins, &c. which are oxidised with great difficulty, should be burnt with lead chromate or in extreme cases with lead chromate containing 10 p.c. of potassium bichromate. The chromate is precipitated by adding potassium bichromate to a solution of lead nitrate, washed, dried, fused, and then granulated. It is heated immediately before being used, and the tube is filled in the same manner as with copper oxide in B. The efficiency of the lead chromate depends mainly on the fact that at a high temperature it fuses. After being used it is heated with nitric acid in order to remove the reduced oxides, and is washed, dried, and re-fused.

Carbon and hydrogen in presence of nitrogen, halogens, &c. When nitrogen is present it is partly converted into nitrogen oxides, which are absorbed by the potash. In order to avoid this source of error, the front of the tube contains plugs of copper wire gauze or a layer of granulated metallic copper 12 to 15 cm. in length reduced in carbonic oxide (v. p. 15). The copper is heated to redness throughout the operation, and the nitrogen oxides are decomposed with absorption of oxygen and liberation of nitrogen.

Perkin (C. J. 1880, 457) employs precipitated manganic oxide made into a paste with a saturated solution of potassium chromate containing 10 p.c. of dichromate, dried and granu-

lated. A layer of this mixture 15 cm. long is placed in the front of the tube and heated to 200–250°C. All nitrogen oxides are absorbed, but if the mixture is heated too strongly they are partially expelled. After each analysis the manganic oxide is heated more strongly whilst a current of air is passed through the tube, and the nitrogen oxides are more or less completely driven off.

The halogens, when present, form haloid copper salts which are somewhat volatile and are liable to be carried into the absorption apparatus. In such cases the front layer of copper may be replaced by silver foil or gauze, which decomposes the nitrogen oxides and also absorbs the halogens. Compounds of this kind may also be burnt by means of lead chromate, as in C., or a mixture of the substance with lead chromate may be placed in a porcelain boat and burnt in a current of oxygen in the usual way.

Sulphur forms sulphur dioxide, which is absorbed by the potash. Compounds containing this element may be burnt with lead chromate, care being taken that the front of the tube is not too hot; or the front of the tube may contain a somewhat longer layer of manganic oxide and potassium chromate, the front half being kept at 200–250° to absorb nitrogen oxides whilst the rear half is heated to dull redness and absorbs the sulphur dioxide (Perkin, *loc.*).

**Nitrogen.** This element is determined in the form of ammonia (Will and Varrentrapp, Ruffe, Kjeldahl), or in the form of nitrogen gas, which is collected and measured, the weight being calculated from the volume (Dumas, Maxwell Simpson).

D. *Will and Varrentrapp's method.* The substance is heated with soda-lime and the nitrogen is evolved as ammonia, which is absorbed in hydrochloric acid and estimated by means of platinum or by titration. This method is not applicable to azo-, diazo-, nitro-, or nitroso-derivatives, nor to certain albuminoid substances.

Soda-lime is prepared by slaking 2 parts of good quicklime with a strong solution of 1 part of sodium hydroxide free from nitrates or sulphates. The mixture is dried by heating in an iron vessel, granulated, and preserved in well-closed bottles. A mixture of equal parts of calcium hydroxide and anhydrous sodium carbonate may also be used.

A glass tube about 50 cm. long and 12 mm. diameter, sealed at one end, is filled to a depth of about 5 cm. with a mixture of anhydrous oxalic acid and granular soda-lime, and a short plug of recently ignited asbestos is inserted. The substance is intimately mixed with sufficient finely powdered soda-lime to form a layer about 15 cm. long, and is quickly introduced into the tube. The mortar is rinsed with a small quantity of soda-lime, which is also put in the tube, and the latter is then filled with granular soda-lime to within 5 cm. from the end and a loose asbestos plug inserted. The tube is tapped to form a channel over the powdered soda-lime for the escape of the gases, and is placed in a furnace, which may be considerably shorter than that used in the estimation of hydrogen and oxygen. The combustion tube is attached by means of a perforated cork to an apparatus for

absorbing the ammonia. This may consist of the bulbs originally devised by Will and Varrentrapp, or of an ordinary bulb U-tube. Winkler has devised a combination of bulb and flask which is especially convenient for estimations by titration, since the liquid need not be transferred. Ordinary dilute hydrochloric acid or a definite volume of standard acid is placed in the bulb. The tube is gradually heated to redness, beginning at the end near the U-tube, and when decomposition is complete the oxalic acid at the back is heated and the ammonia in the tube is driven out by the current of carbonic oxide and carbonic anhydride. The excess of acid is then determined by standard alkali; or the liquid is evaporated with platinum chloride as in an ordinary estimation of ammonia, and the precipitate is washed with ether containing a small quantity of alcohol, dried, heated in a crucible till completely decomposed, and the nitrogen calculated from the weight of the residual platinum;  $Pt = N_2$ . The nitrogen frequently forms volatile bases other than ammonia, and hence the platinum precipitate cannot be weighed as such. The ratio of platinum to nitrogen is, however, the same in all cases. The precipitate is washed with ether because if such bases are present it may be soluble in alcohol.

It is important that the front part of the tube be heated sufficiently to secure complete decomposition, but the temperature must not be too high, otherwise part of the ammonia itself is decomposed and the results are too low. Substances rich in nitrogen should be mixed with some pure sugar in order to dilute the ammonia and prevent too rapid absorption.

E. *Ruffe's method* (C. J., 1881, 87). This is a modification of the preceding method, with a view to make it applicable to nitro-derivatives and similar compounds, and to albuminoids. The soda-lime is mixed with a powerful reducing agent in the form of sodium thiosulphate, and the substance itself is mixed with sulphur and charcoal. The soda-lime is prepared by adding a solution of 160 grams of caustic soda in an equal weight of water, to 56 grams of finely-powdered quicklime from marble, and drying the mixture.

The combustion tube is of iron, about 60 cm. long and 15 mm. diameter. 21 grams of crystallised sodium thiosulphate is mixed with 18 grams of soda-lime and 5 grams of this mixture is placed in the tube. The substance, previously mixed with an equal weight of a mixture of finely-powdered sulphur and wood charcoal in equal proportions, is mixed with 30 grams of the soda-lime and thiosulphate and the mixture placed in the tube, followed by the remainder of the soda-lime and thiosulphate. 18 grams of ordinary soda-lime is then introduced, and finally a plug of asbestos. The tube is placed in the furnace and tapped to produce a channel for the gases. The mixture fills the tube to within about 20 cm. from the open end, which is connected with the usual absorption apparatus. The tube is gradually heated to redness, beginning at about 10 cm. from the front end. The layer of ordinary soda-lime in the front of the tube absorbs hydrogen sulphide which would otherwise escape.

Arnold finds (B. 18, 806) that, except in the case of diazo-compounds, this method is generally applicable. The results, however, are sometimes too low in consequence of the formation of channels in the tube, and he proposes the following modification: 0.5-0.3 grams of the substance, according to its richness in nitrogen, is mixed with a mixture of 2 parts anhydrous sodium thiosulphate, 1 part soda-lime, and 1 part sodium formate, in sufficient quantity to form a layer 12-15 cm. long. The tube is filled with a layer of the reduction mixture 5 cm. long, then with the mixture containing the substance, then a layer 15-20 cm. long of a mixture of 2 parts soda-lime and 1 part each of sodium formate and thiosulphate, and finally 5 to 10 cm. of ordinary soda-lime. No channels need be formed, since the heated mass is porous and allows the passage of the gas. The temperature must not be sufficient to cause partial fusion.

**F. Dumas' method.** In this process the hydrogen and carbon are burnt by means of cupric oxide and the liberated nitrogen collected and measured. A glass tube 80 cm. long, 12 to 15 mm. diameter, sealed like a test tube at one end, is filled to a length of 12-15 cm. with dry sodium hydrogen carbonate, 4 cm. of cupric oxide is added, and then an intimate mixture of the substance (0.3 to 0.6 gram) with cupric oxide, then the cupric oxide used to clean the mortar, a layer of granular cupric oxide, and finally a layer of reduced granulated copper or copper-wire gauze not less than 15 cm. in length. The tube is connected by means of a cork and bent tube with an apparatus for collecting the nitrogen. The sodium carbonate is first heated until all air is expelled and the issuing gas is completely absorbed by potash solution. The copper is then heated to redness, the heat being gradually applied to the whole tube as far as the carbonate. When combustion has ceased the carbonate is again heated until all the nitrogen has been expelled.

The most convenient form of apparatus for collecting the nitrogen is that devised by H. Schiff (Fr. 7, 430), or a similar form described by Groves (C. J. 1880, 500). The former consists of a burette fitted with a heavy foot and provided with a stopcock *c* at the top. Close to the bottom is a tubulus *b* inclined at an angle of about 45°, and on the other side is another tubulus *a* connected by means of a caoutchouc tube previously soaked in paraffin with a globular reservoir *B* which is attached to the burette by a clip, and the height of which is readily adjusted. Mercury is poured into the burette through the lower tubulus to a height of 2 or 3 mm. above the lower opening, and the reservoir is then filled with a solution of

potash in its own weight of water, the lower tubulus being closed with a cork. The stopcock is opened and the reservoir raised until the burette is completely filled with the potash solution. The stopcock is then closed and the reservoir lowered to the bottom of the burette. The tubulus may now be opened without the mercury or potash solution being forced out. When the air has been expelled from the combustion tube the end of the delivery tube is inserted through the tubulus and the nitrogen collected. At the close of the operation the temperature of the gas is allowed to become constant, the reservoir is raised so that the level of the liquid is the same as in the burette, and the volume of the nitrogen is read off together with the temperature and the height of the barometer. The weight of the nitrogen, *P*, is then calculated from the volume by means of the formula

$$P = \frac{V(B-f)0.001256}{(1+0.00366t)760}$$

where *V* is the observed volume, *B* the height of the barometer, *f* the tension of aqueous vapour at the temperature *t*, and 0.001256 the weight of 1 c.c. of nitrogen at 0° and 760 mm.

A table giving the values of  $\frac{0.001256}{(1+0.00366t)760}$  for different temperatures has been calculated by J. T. Brown (Fr. 4, 450).

Gatterman (Fr. 24, 57) collects the nitrogen in an apparatus similar to Schiff's, but not graduated. A bent tube of small diameter completely filled with water is attached to the jet of the burette by means of caoutchouc tubing. By closing the lower tubulus, raising the potash reservoir and opening the stopcock, the gas is driven over into a graduated tube standing over water, and is measured. The error due to the unknown vapour tension of the potash solution is thus avoided, but the vapour tension of the water at the particular temperature must of course be taken into account. Other forms of apparatus are described by Zulkowsky (A. 182, 296. Roscoe and Schorlenmer's Chemistry, 3, pt. 1, 74) and Schwarz (B. 13, 771).

**G. Maxwell Simpson's modification of Dumas' method** (C. J. 6, 290; A. 95, 74). In order to avoid the formation of carbonic oxide and nitric oxide the substance is burnt with a mixture of cupric oxide and mercuric oxide. Into a tube similar to that used in Dumas' method is introduced about 12 grams of manganese carbonate or granulated magnesite mixed with 2 grams of precipitated mercuric oxide, followed by a plug of asbestos. Another gram of mercuric oxide is introduced and then an intimate mixture of 0.5 gram of the substance with 45 parts of a previously prepared and thoroughly dry mixture of 4 parts ignited cupric oxide and 5 parts precipitated mercuric oxide. The mortar and the sides of the tube are rinsed with a similar mixture and another asbestos plug is introduced. A layer of granular cupric oxide about 9 cm. in length and a layer of not less than 20 cm. granulated copper, kept in position by another asbestos plug, fill the remainder of the tube. After the air has been expelled by heating the manganese carbonate or magnesite, the tube is gradually heated to redness, beginning from the front. The metallic copper not only decomposes nitrogen oxides but

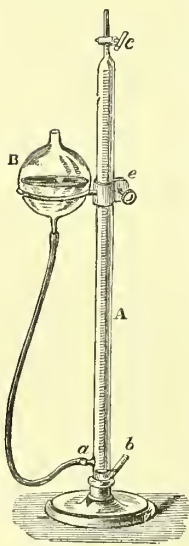


FIG. 23.



also absorbs the excess of oxygen. The gas is collected as in Dumas' method, the magnesite or manganese carbonate providing the carbon dioxide.

Various modifications of Dumas' process have been proposed. Thudichum and Wanklyn use a mixture 5 parts normal sodium carbonate and 13 parts fused potassium bichromate in place of sodium hydrogen carbonate. Groves (*l.c.*), with a view to use the same tube repeatedly, places the mixture of carbonate and bichromate in a small tube connected with the combustion tube by an indiarubber joint. The portion of the cupric oxide mixed with the substance is separated from the layer remaining always in the tube by means of a tight plug of asbestos and copper gauze, the latter keeping a free passage for the gas.

The combustion tube may be open at both ends, the rear being connected with an apparatus for generating carbon dioxide, but special precautions must be taken to obtain this gas free from air (*v.* Warington, C. J. 1882, 346).

In both Dumas' method and Simpson's modification the combustion tube may be drawn out at the front end and connected with a Sprengel mercury pump by glass tubing joined by short pieces of caoutchouc tubing, the joints being surrounded by short wide tubes filled with water or glycerol. A bulb is blown on the

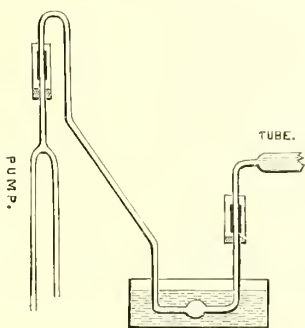


FIG. 24.

horizontal part of the glass tube at the end near the combustion tube, and this bulb is kept cool during the operation, and serves to condense the water which is formed. The combustion tube is made vacuum, and when no more air issues from the end of the pump, the combustion is conducted in the ordinary way, the gas which is evolved being pumped out by the Sprengel pump and collected in a suitable tube. No magnesite need be used. The copper oxide keeps the exhausted tube from collapsing when heated.

In many cases, especially with nitro-derivatives, the gas evolved is a mixture of nitrogen with nitric oxide, the latter being sometimes present in considerable quantity. It is advisable, therefore, to transfer the gas to a suitable apparatus and estimate the nitric oxide by absorption with ferrous sulphate solution (*v.* *Gas analysis*).

Liquids in which nitrogen is to be determined may be inclosed in bulbs which are dropped into the combustion tubes as in the determination of hydrogen and oxygen.

The copper oxide used in nitrogen determinations should be prepared by heating metallic copper in air and never by ignition of the nitrate, since in the latter case it is apt to contain basic nitrates which evolve nitrogen on heating.

The copper used in nitrogen determinations &c. should not be reduced in hydrogen, since it is liable to occlude this gas. It may be reduced in the mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with strong sulphuric acid. Plugs of copper gauze may also be reduced by heating them to redness and dropping them into a test tube containing a few drops of formic acid or methyl alcohol. The reduced copper is carefully dried at 100°–110°.

When no carbonate is used and the gas is simply pumped out of the tube and collected over mercury, it consists of a mixture of carbon dioxide and nitrogen. If the former is estimated by absorption with potash, a determination of the carbon may be combined with that of nitrogen.

Jannasch and Meyer have described a method for the simultaneous estimation of carbon, hydrogen, and nitrogen (*B.* 19, 949; *A.* 233, 375; *Fr.* 26, 86).

*H. Kjeldahl's method* (*Fr.* 22, 366). The substance is heated with concentrated sulphuric acid to a temperature approaching the boiling point of the latter, and when decomposition is complete, an excess of solid potassium permanganate is added. The nitrogen is thus converted into ammonium sulphate, which is then distilled with excess of alkali and the ammonia collected and estimated. This method is economical, requires no combustion furnace or special apparatus, is rapid, and requires comparatively little attention, so that a large number of determinations can be carried on at the same time. The substance need not be in a very fine state of division, and the method is especially suitable for liquid and pasty substances such as extracts.

0.3 to 1.0 gram of the substance, according to its richness in nitrogen, is placed in a round hard glass flask of about 100 c.c. capacity, with a long neck, mixed with 10 c.c. of the strongest sulphuric acid free from ammonium sulphate, and heated gradually to the boiling-point of the acid, without, however, actually entering into ebullition, the flask being inclined in order to prevent loss by spurling. When the black liquid has become light coloured but not necessarily colourless, the lamp is removed and finely powdered potassium permanganate is added very gradually until the liquid has a dark-green or bluish-green colour. It is then gently heated for four or five minutes, allowed to cool, and diluted with water. After again cooling, it is transferred to a flask of 600–700 c.c. capacity, mixed with an excess of soda solution of sp.gr. 1.3, free from ammonia, and connected with a condenser, the tube of which is bent over so that the flask is inclined and no liquid can be spurted into the condenser. The liquid is then boiled for about half an hour, and the ammonia absorbed in standard acid and estimated by titration as in an ordinary determination of ammonia (*v.* ACIDIMETRY).

It is important that the sulphuric acid employed for these determinations should be protected from ammonia, and the soda solution

should be well boiled in order to expel any ammonia which it may contain. The purity of the reagents is best ascertained by making an experiment with pure sugar. If a small quantity of ammonia is present the same quantity of the reagents should be used in each experiment, and a correction made for the ammonia which they contain.

In order to prevent bumping during distillation a small piece of zinc may be placed in the flask, but it is essential that the soda should be free from nitrites and nitrates, which would be reduced and yield ammonia.

The time required for the operation may be considerably shortened by using sulphuric acid containing sulphuric anhydride or phosphoric anhydride.

The method as thus carried out is applicable to all substances which can be analysed by Will and Varrentrapp's process, and to many others. It does not, however, estimate the whole of the nitrogen in nitro- and azo-derivatives, nitrates, nitrites, &c. Various modifications have been made with a view to shorten the time required and to make the process more generally applicable.

Heffter, Hollrung, and Morgen (Z. 8, 432) treat 1.0 to 1.5 gram of substance with 20 c.c. of a mixture of 4 vols. ordinary sulphuric acid and 1 vol. of fuming acid, and 2 grams of phosphorus pentoxide. Kreisler (Fr. 24, 453) uses sulphuric acid containing 200 grams of phosphorus pentoxide per litre.

Wilfarth (C. C. [3] 16, 17 and 113) finds that the oxidation of the organic matter takes place much more rapidly in presence of certain metallic oxides. Mercuric oxide is the most efficient, but cupric oxide answers almost equally well. The former produces ammonia derivatives which are not readily decomposed by soda, and hence the alkaline liquid must be mixed with some potassium sulphide to decompose the mercury compounds. The mercuric sulphide formed makes the liquid boil regularly without the addition of zinc. Ulsch recommends the use of ferrous sulphate instead of potassium sulphide; it may be added before the soda.

Warrington (C. N. 52, 162) removes nitrites and nitrates by boiling with ferrous sulphate and hydrochloric acid.

With a view to secure the reduction of nitro-derivatives &c., and thus make the process generally applicable, Asboth (C. C. [3] 17, 161) mixes 0.5 gram of the substance with 1 gram of pure sugar in the case of readily oxidisable compounds, and with 2 grams of benzoic acid in the case of nitrates and similar derivatives. Most probably the benzoic acid first forms nitro-derivatives, which are afterwards reduced. He adds Rochelle salt with the caustic soda in order to prevent precipitation of manganese &c., and thus avoids bumping during distillation. With these modifications the method is applicable to all nitrogen compounds except those of the pyridine and quinoline series. E. Arnold (*ib.* p. 337) uses 0.5 gram anhydrous cupric sulphate and 1 gram metallic mercury in place of the oxides as recommended by Wilfarth, and heats 1 gram of the substance with these and 20 c.c. of sulphuric acid containing 20-25 p.c. of phosphorus pentoxide.

C. Arnold (Ar. Ph. [3] 24, 785) confirms Asboth's statements, but finds that in addition to pyridine and quinoline compounds, azo-derivatives and nitrites yield unsatisfactory results. He heats 0.5 gram of substance with 0.5 gram anhydrous cupric sulphate, 1 gram of metallic mercury, 2 grams phosphorus pentoxide, 1 gram of sugar, and in case of nitrates, &c., 2 grams of benzoic acid, and 20 c.c. of sulphuric acid.

Reitmaier and Stutzer (Rep. Anal. Chem. 5, 232; Fr. 25, 582) use about 0.7 gram of mercuric oxide and 20 c.c. of sulphuric acid, with a small fragment of paraffin in the case of substances rich in fat. They regard the use of phosphorus pentoxide as unnecessary, and the use of fuming sulphuric acid as undesirable on account of its liability to contain nitrogen oxides.

Jodblauer (C. C. [3] 17, 433) uses phenol-sulphonic acid in place of benzoic acid, and reduces with zinc-dust. He thus obtains good results even with nitrates. Reitmaier and Stutzer (Rep. Anal. Ch. 7, 4) find that the nitrate must be somewhat finely divided. 0.5 to 1.0 gram of the substance is mixed with 50 c.c. of sulphuric acid containing 20 grams of phenol per litre, allowed to stand for a short time with occasional agitation, mixed with 2-3 grams of dry zinc powder and 1 or 2 drops of metallic mercury, and heated in the usual way. Conversion into ammonium sulphate requires one and a half hours.

When mercury or copper salts are present the addition of potassium permanganate is frequently unnecessary. It is safer, however, not to omit it.

The literature of nitrogen determinations is extremely voluminous. Summaries of the most recent contributions will be found in Fr. 23, 551; 24, 439; 25, 424 and 571; 26, 249; and C. N. 57, 62, *et seq.* In addition to the references already given, papers relating to Kjeldahl's process may be found in Fr. 24, 199, 388, and 393; 25, 149 and 155; 26, 92; 27, 222 and 398.

#### Chlorine, bromine, and iodine.

*By lime.* A tube about 40 cm. long and 7 mm. diameter, sealed at one end like a test tube, is filled to a depth of 5 cm. with pure granulated quicklime. The substance is weighed into the tube and mixed with finely-powdered lime by means of a copper wire twisted at the end like a corkscrew. The wire and tube are rinsed with lime, the tube is filled to within 5 cm. of the open end with granulated lime, and a loose plug of asbestos or glass wool is inserted. It is then fitted with a cork carrying a narrow tube, the end of which just dips under mercury in a crucible or small beaker. The tube is gradually heated to redness from the front. When cold the contents of the tube are dissolved in water slightly acidified with nitric acid, filtered, and the halogen precipitated by silver nitrate.

In the case of iodine the substance is dissolved in water, filtered, mixed with silver nitrate, and finally acidified, in order to avoid liberation of iodine.

When the substance contains nitrogen, cyanides may be formed; but this is avoided by using pure soda-lime in place of lime. If the lime contains sulphates, some sulphide is liable

to be produced. On the preparation of pure lime see Fr. 4, 51 and 15, 5.

Liquids are contained in small bulbs with capillary openings, which are dropped into the tube before filling up with lime. The tube must be very gradually heated, and should be longer than usual.

*Carius's method* (A. 116, 1; 136, 129; B. 3, 697). The substance is oxidised by heating with nitric acid in sealed tubes in presence of silver nitrate. In many cases acid of sp.gr. 1.2 and a temperature of 120–200° will suffice; but substances which are more difficult to oxidise require acid of sp.gr. 1.42, mixed in special cases with some potassium bichromate, or the fuming acid of sp.gr. 1.5 may be used. If necessary the tubes may be heated as high as 300°. The quantity of acid used should not be more than twice that theoretically required for complete oxidation, and the tube must not contain more than 4 grams of nitric acid for each 50 c.c. of its volume. If the operation is prolonged, it is desirable to reduce the pressure in the tube by opening it from time to time by heating the capillary end of the previously cooled tube in a flame until it softens, when the gas forces its way out.

The weighed substance is inclosed in a narrow tube of thin glass of such length that its mouth projects above the nitric acid in the tube, and the acid does not come in contact with the substance until the tube is sealed. The tubes used should be about 15 mm. in diameter and 1.5–2 mm. thick in the glass. After introduction of the substance they are drawn out to a capillary tube with thick walls, which is then sealed. After being heated any attempt to open them with a file would be highly dangerous. They should be wrapped in a cloth and opened by softening the tip of the capillary end in a flame, care being taken that the tube is held in such a way that the liquid cannot be forced out.

The silver salt formed is separated and treated in the usual way.

#### Sulphur and phosphorus.

*Non-volatile substances.* Pure potash is fused in a silver dish with about one-sixth its weight of potassium nitrate and a little water. When cold the substance is weighed into the dish, which is again heated, the substance being mixed with the potash by means of a silver spatula. When oxidation is complete the mass is allowed to cool, and is then dissolved in water acidified with hydrochloric acid, and the sulphuric or phosphoric acid estimated in the usual way.

*Carius's method* is carried out exactly as in the estimation of the halogens. Sulphur is oxidised to sulphuric acid and phosphorus to phosphoric acid. It is advisable to remove the greater part of the nitric acid before precipitating as barium sulphate or magnesium ammonium phosphate.

Another method applicable to volatile and non-volatile substances is as follows:—Into a combustion tube 40 cm. long, sealed at one end, is introduced 2–3 grams of pure mercuric oxide, then a mixture of the substance with equal proportions of mercuric oxide and pure anhydrous sodium carbonate, and the remainder of the

tube is filled with sodium carbonate mixed with a small quantity of mercuric oxide. The open end of the tube is closed by a cork carrying a glass tube dipping under water, in which the mercury is condensed. The tube is carefully heated so that the front layer of sodium carbonate is red hot before the substance begins to volatilise. The substance is then rapidly heated so that decomposition is complete in about fifteen minutes, and finally the mercuric oxide at the rear end of the tube is heated until oxygen gas issues from the end of the delivery-tube (Russell, C. J. 1854, 212; J. Pr. 64, 230). The contents of the cooled tube are dissolved in water, a small quantity of bromine water added to oxidise any sulphide, the solution acidified with hydrochloric acid, boiled to expel bromine, and the sulphuric acid or phosphoric acid estimated in the usual way.

Many non-volatile substances may be oxidised by heating with pure concentrated potash solution, diluting with twice the volume of water, and treating with a current of chlorine. After complete oxidation the solution is acidified, heated to expel chlorine, and the sulphuric or phosphoric acid determined.

**Oxygen.** No satisfactory method has yet been devised for the direct determination of this element, and it is usually estimated by difference (*v. v.* Baumhauer, A. 90, 228; Fr. 5, 141; Stromeyer, A. 117, 247; Mitscherlich, Fr. 6, 136; 7, 272; 13, 74, and 15, 371; Ladenburg, A. 135, 1; Maumené, C. R. 55, 432; and Cretin, Fr. 13, 1).

*Calculation of results.*—The quantity of hydrogen present is obtained at once from the relation  $H = \frac{\text{weight of water}}{9}$ , and that of the

carbon from the relation  $C = \frac{\text{carbon dioxide}}{3.6364}$ , and the percentage composition is calculated in the usual way.

In order to obtain the empirical formula the percentage numbers are divided by the atomic weights of the respective elements, and the numbers thus obtained are the ratios of the number of atoms of each element in the molecule. For example, in the case of theine—

Carbon . . . . .	49.51
Hydrogen . . . . .	5.22
Nitrogen . . . . .	28.99
Oxygen . . . . .	16.28
	<hr/>
	100.00

$$\frac{49.51}{12} = 4.13; \quad \frac{5.22}{1} = 5.22; \quad \frac{28.99}{14} = 2.07; \quad \frac{16.28}{16} = 1.02.$$

These ratios are approximately 4:5:2:1, and hence, apart from all other considerations, the simplest formula for theine is  $C_4H_5N_2O$ .

#### Gas analysis.

The experiments of Gay-Lussac established long ago the value, from a scientific point of view, of the determination of the volumetric composition of gases and the products formed by their interaction; but it is only within recent times that the methods of gas analysis have been applied to any great extent for technical purposes. The value of such determinations is now generally recognised on account of the informa-



tion which they give respecting the efficiency of combustion, the progress of operations in which gases are consumed or produced, and the like.

With few exceptions the volumetric and not the gravimetric composition of the gas is required, and the measurements are essentially measurements of volumes. The gas to be examined is confined over mercury or water in a suitable measuring apparatus, and its composition is determined—(1) by treatment with appropriate absorbing reagents and measurement of the contraction produced; (2) by exploding with oxygen or hydrogen and measuring the contraction; (3) by exploding with oxygen or hydrogen, measuring the contraction, and then treating with absorbing reagents, and measuring the second contraction. Sulphur dioxide and some other gases soluble in water are estimated by titration, a definite volume of the gas being drawn through a measured quantity of a standard solution, the excess of which is afterwards determined.

The highly refined and accurate methods of gas analysis employed for purposes of research are of little value for technical purposes on account of the length of time required for their execution. Information respecting these methods may be found in Bunsen's *Gasometrische Methoden*, 2nd ed. 1877; Sutton's *Volumetric Analysis*, 5th ed. 1887; Dittmar's *Exercises in Quantitative Analysis*, 1887; and Watts' *Dictionary*, v. also Thomas (C. J. 35, 213), and Meyer and Seubert (C. J. 45, 581). In this article only those methods will be described which are available for technical purposes.

*Measurements.*—The volume which a given mass of gas occupies depends on the temperature, the pressure, and the proportion of moisture which it contains. The temperature is ascertained by means of a thermometer attached to or suspended near to the measuring vessel. Measurements are usually made under atmospheric pressure, and this is determined by means of a barometer placed in the room in which the analysis is made. The siphon barometer is a

convenient form of instrument for the purpose, and should stand on the table close to the gas apparatus. In case the level of the mercury or water in the measuring tube is higher than that in the trough or the attached tube, the true pressure upon the gas is given by the height of the barometer minus the difference between the mercury level inside and outside the tube. If water is used, the height of the water column divided by 13.6 gives the height of the corresponding column of mercury with sufficient accuracy. It is better to eliminate this correction by adjusting the liquid so that it is at the same level both inside and outside the tube, which is easily done.

The gas must be either perfectly dry or saturated with moisture. If an indefinite quantity of water vapour is present, accurate measurements are impossible. It is more convenient to measure the gas when moist, and hence if the gas is confined over mercury a few drops of water are introduced when the tube is filled with the mercury and this water is taken up by the gas. Under these conditions the surrounding pressure is balanced partly by the gas and partly by the aqueous vapour which it contains, and in order to ascertain the pressure which the gas itself is under, the tension of aqueous vapour at the particular temperature must be subtracted from the height of the barometer. The formula for reducing the volume of gas to the standard temperature and pressure (0° and 760 mm.) is—

$$V_0 = \frac{V + 273 \times (B - f)}{(273 + t) \times 760} \quad \text{or} \quad V_0 = \frac{V \times (B - f)}{(1 + 0.00366t) \times 760}$$

in which  $V$  is the actual reading,  $t$  the temperature,  $f$  the tension of aqueous vapour at the temperature  $t$ , and  $B$  the height of the barometer. The reduction of the height of the barometer to 0° is necessary for accurate calculation, but may usually be omitted. The following table, abbreviated from Bunsen's *Gasometrische Methoden*, gives the value of  $1 + 0.00366t$  for the ordinary range of temperature:—

$t^\circ$	Number	Log	$t^\circ$	Number	Log	$t^\circ$	Number	Log
0°	1.00000	0.00000	11	1.04026	0.01714	21	1.07686	0.03216
1	1.00366	0.00159	12	1.04392	0.01867	22	1.08052	0.03363
2	1.00732	0.00317	13	1.04753	0.02019	23	1.08418	0.03510
3	1.01098	0.00474	14	1.05124	0.02170	24	1.08784	0.03656
4	1.01464	0.00631	15	1.05490	0.02321	25	1.09150	0.03802
5	1.01830	0.00788	16	1.05856	0.02471	26	1.09516	0.03948
6	1.02196	0.00943	17	1.06222	0.02621	27	1.09882	0.04093
7	1.02562	0.01099	18	1.06588	0.02771	28	1.10248	0.04237
8	1.02928	0.01253	19	1.06954	0.02921	29	1.10614	0.04381
9	1.03294	0.01407	20	1.07320	0.03068	30	1.10980	0.04524
10	1.03660	0.01561						

When the estimations are made rapidly, and only approximate results are required, the corrections for temperature and pressure are omitted, since it may be assumed that they remain constant during the analysis.

The following plan, described by Winkler, renders the use of the barometer and thermometer unnecessary, and makes the calculation much simpler. It is an adaptation of William-

son and Russell's method of always measuring the volume of the gas at the same degree of elasticity. A tube about 1 metre long, closed at one end and graduated to 120 c.c. in tenths, is moistened internally with a few drops of water, and mercury is poured in in such quantity that when the tube is inverted the mercury stands somewhat higher than 100. The volume which 100 c.c. of air measured at standard temperature

and pressure should occupy under the conditions described is calculated from the expression—

$$V = \frac{(760-4.5)100 \times (273+t)}{273(B-f)} \quad \text{or} \quad \frac{(760-4.5)100 \times (1+0.00366t)}{B-f}$$

and air is carefully introduced into the tube until, when the mercury is at the same level inside and outside the tube, it stands exactly at the calculated volume. The tube now contains a quantity of gas saturated with moisture, which, under standard conditions, would occupy 100 c.c., but its actual volume varies in the same ratio as the volume of gas to be measured. The two tubes are allowed to stand side by side, and when the levels have been properly adjusted in each case the volume of the gas to be measured and the volume of the air in the comparison tube are read off. The volume (under standard conditions) of the gas under examination is obtained by the proportion—

$$V : V_0 :: V_1' : V_0'$$

in which  $V$  is the actual volume of air in the comparison-tube;  $V_0$ , its volume under standard conditions, which is always 100;  $V_1$ , the observed volume of the gas to be measured; and  $V_0'$ , is volume under standard conditions.

During the operations the temperature should be kept as constant as possible, and the readings should be taken rapidly, otherwise the proximity of the body will cause variations in the temperature of the gas. It is an advantage to have the measuring tube surrounded by a wider tube which is filled with water. The most accurate method is to take the readings through a carefully levelled telescope (a cathetometer) at a distance of five or six feet. This also avoids parallax (*v. p.* 140). The measuring-tube must be vertical, and when water is the confining liquid, sufficient time must be given for the liquid to run down the sides of the tube. Not unfrequently this requires several minutes.

#### Reagents.

All liquid reagents should be saturated with the gases which they do not absorb chemically. It is desirable that the tensions of these gases in the liquids should be approximately equal to their tensions in the gases which are to be analysed, in order to avoid exchanges between the gas and the absorbing liquid. This is best secured by going through the process two or three times without making measurements whenever the pipettes have been freshly filled. Liquids used for the analysis of, say, flue gases, should not be used for gases of a different character, *i.e.* which contain the constituents in very different proportions.

*Bromine water* is used for absorbing olefines. It should be well saturated with bromine and be kept in the dark.

*Cuprous chloride* is made by dissolving 50 grams of cupric oxide in hydrochloric acid, adding 50 grams of copper, and boiling for some time with as little exposure to air as possible. The solution is then diluted to 1,000 c.c. with hydrochloric acid of sp.gr. 1.12, and allowed to remain in contact with metallic copper in a closed vessel until the solution becomes colourless. This solution attacks mercury rapidly.

*Cuproso-ammonium chloride* is obtained by dissolving cuprous chloride in ammonia. It does not attack mercury.

*Hydrogen* is obtained by the action of dilute sulphuric acid on pure zinc. The granulated zinc may be placed in a small bottle fitted with a capillary delivery tube which can be closed by a tap or pinchcock. The bottle has a tubulus at the bottom, and is connected by a caoutchouc tube with a similar bottle containing dilute sulphuric acid. The latter bottle is raised so that the acid runs on the zinc, and the action is allowed to proceed until the air is completely expelled from the first bottle. The tap is then closed, and the acid is driven back into the second bottle by the pressure of the hydrogen. It is advisable to keep the second bottle at a slightly higher level than the first to avoid any chance of air leaking in. One of Hempel's tubulated absorption bulbs answers admirably (*p.* 159). The zinc is attached to a cork, which is inserted in the tubulus of the first bulb, and the acid is introduced. When all air is expelled the capillary tube is closed, and the acid is driven up into the second bulb, so that the pipette is always charged with hydrogen under pressure.

*Oxygen* is obtained in a pure state by heating potassium chlorate *without* manganese dioxide. The powdered chlorate is contained in a glass bulb, the neck of which is drawn out to form a narrow delivery tube.

*Phosphorus* is employed in the form of narrow sticks, which are made by melting it under warm water and drawing it up into narrow glass tubes. The upper ends of the tubes are closed by the finger and they are plunged into cold water, when the phosphorus solidifies. It may also be used in a granular form, obtained by shaking the phosphorus vigorously with warm water in a well-closed flask until it solidifies.

*Potash* (or *soda*) for Orsat's apparatus is dissolved in 3 parts of water and the solution kept in well-stoppered bottles. Hempel uses a solution of potash in two parts of water, which will absorb forty times its volume of carbon dioxide. It may, however, be used somewhat more dilute, and is then less liable to attack the glass.

*Pyrogallol* is kept in the solid state, and only dissolved immediately before being used. Orsat recommends a solution of 25 grams of pyrogallol in a small quantity of hot water, mixed with 150 c.c. of a solution of 1 part of caustic soda in 3 parts of water. Hempel uses a mixture of 25 c.c. of a 20 p.c. solution of pyrogallol with 75 c.c. of potash solution of 33.3 p.c. This quantity will absorb 200 c.c. of oxygen.

*Sulphuric acid* of sp.gr. 1.84 is used as a drying agent and for the absorption of nitrogen oxides. Acid of the same strength mixed with so much sulphuric anhydride that it remains liquid at the ordinary temperature but solidifies if cooled, is used for absorbing ethylene and other hydrocarbons.

*Water*, which is very largely used for confining the gases, should be well saturated with air, but should not contain carbon dioxide. Distilled water is preferable, but any potable water of good quality may be used.

*Standard solutions* used in the estimation of gases by titration are known as *normal gas solutions* when they are of such strength that 1 c.c. of the solution is equivalent to 1 c.c. of the gas under standard conditions. A normal gas solu-



tion of iodine for the estimation of sulphur dioxide would contain 11.333 grams of iodine per litre, and the thiosulphate solution used in conjunction with it would be of equivalent strength.

In many cases it is the weight of the absorbed constituent per cubic metre or cubic foot of gas that is required, and the ordinary standard solutions may be used.

#### *Methods of estimation.*

##### *Ammonia, by titration.*

**Benzene**, by absorption in fuming nitric acid boiling at  $86^{\circ}$ , the nitrogen oxides being afterwards removed by potash. Fuming nitric acid also absorbs carbon dioxide and carbon monoxide. Like the olefines, benzene is absorbed by fuming sulphuric acid and by bromine water, and in fact no absorption method is at present known by means of which benzene and the olefines can be separated (B. 21, 3131).

**Carbon dioxide**, by absorption in potassium or sodium hydroxide.

**Carbon monoxide**, by absorption in a saturated solution of cuprous chloride in hydrochloric acid or ammonia. It seems (B. 20, 2754) that these solutions are liable to give off part of the dissolved carbon monoxide, especially after they have been used repeatedly. The error is less with the ammoniacal solution, and is reduced if the solution remains in contact with the gas for some time. The cuprous chloride solution should always be tolerably fresh, and should be saturated with hydrogen, nitrogen and the other gases which usually occur with carbonic oxide (B. 21, 898). If the amount of carbon monoxide is small it should be converted by combustion (*v. Hydrogen*) into carbon dioxide, which is afterwards absorbed by potash. If the amount of carbon monoxide is large, the greater part may be absorbed by cuprous chloride and the remainder removed by combustion and absorption.

**Hydrogen** is converted into water by combustion with air or oxygen, and the volume of the hydrogen is represented by two-thirds of the contraction consequent upon combustion. If the gas is confined over mercury, an excess of pure oxygen is introduced, the volume read off, and the pressure on the gas reduced considerably below atmospheric pressure by lowering the mercury in the level tube. The lower end of the explosion tube is closed, and combination is initiated by passing a spark from a coil between the platinum wires which are fused into the tube. The pressure is restored to the normal, and when the gas has cooled the volume is again read off.

When the gas is confined over water it is almost impossible to obtain satisfactory combustion, and it is much more convenient to pass the combustible mixture over gently-heated spongy palladium. This is prepared by dissolving about two grams of palladium chloride in a small quantity of water, adding a small quantity of a saturated solution of sodium formate and sodium carbonate until the reaction is alkaline. About 1 gram of long and very soft asbestos fibres is introduced, and the pasty mass is dried at a gentle heat. In this way the asbestos is obtained covered with very finely divided palladium. After being completely dried at  $100^{\circ}$  it is carefully washed with water to remove soluble

salts and again dried. Some of the fibres are moistened and twisted into a thread about a cm. long, which is then introduced into the middle of a stout capillary tube about 15 cm. long and 1 mm. internal diameter, and this tube is bent at a right angle at each end or in any other way convenient for its attachment to the measuring apparatus containing the gas. One end of the capillary is in communication with the graduated tube, and the other with a bulb pipette, filled completely with water, into which the gas is

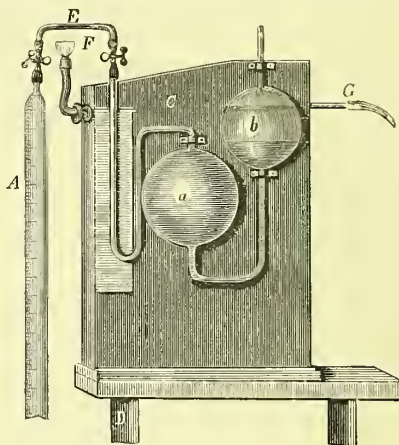


FIG. 25.

passed. A small gas or spirit lamp flame is arranged to heat that part of the capillary which contains the asbestos. When the other gases have been estimated, the mixture of hydrogen and nitrogen which remains is mixed with air by lowering the level-vessel until the pressure is sufficiently reduced, and then putting the measuring tube in communication with the air. The stopcock is then closed, the asbestos very gently heated, and the gas passed slowly through the capillary into the bulb and back again three or four times. When combustion is complete, the volume of the residual gas is measured.

Drehschmidt (B. 21, 3245) prefers a platinum tube 20 cm. long and 2 mm. thick, with a bore 0.7 mm. diameter. The bore is almost closed by the insertion of a palladium wire extending through the whole length of the tube. The tube is attached to a burette and an absorption pipette in the same manner as the glass tube, 5 to 6 cm. is heated to redness by means of a gas flame, and the gas is passed backwards and forwards until there is no further alteration of volume. No explosion occurs even with mixtures of hydrogen and oxygen containing only a slight excess of the latter.

##### *Hydrochloric acid by titration.*

##### *Hydrogen sulphide by titration.*

**Hydrocarbons** other than olefines are estimated by combustion, preferably with oxygen over mercury under reduced pressure. Acetylene and benzene may be burnt over palladium, but require a somewhat high temperature. Methane cannot be burnt in this way even in presence of hydrogen. The combustion of this gas is effected by mixing it with a considerable quantity of air



and aspirating the mixture through a short tube containing cupric oxide heated to redness in a small combustion furnace, the carbon dioxide which is produced being absorbed in standard baryta solution, which is afterwards titrated with standard oxalic acid.

Drehschmidt finds (B. 21, 3249) that a mixture of methane and oxygen can readily be burnt in a platinum tube, as above, if the latter is heated to bright redness. The contraction is observed, and the carbon dioxide formed is removed and the volume again measured.

**Nitric oxide** is converted into peroxide by admixture with oxygen, and the peroxide is absorbed by potash, the excess of oxygen being afterwards absorbed by potash and pyrogallol. Nitric oxide may also be absorbed by a concentrated solution of ferrous sulphate, but this method does not give such satisfactory results.

**Nitrogen peroxide and nitrous anhydride** by titration; by absorption with sulphuric acid of sp.gr. 1.84; or, in absence of carbon dioxide and other absorbable gases, by absorption with potash.

**Olefines**, by absorption with fuming sulphuric acid, acid vapours being removed by potash; or by absorption in bromine water, bromine vapours being afterwards removed by potash.

**Oxygen**, by absorption with alkaline pyrogallol. If the oxygen is present in greater proportion than 20 p.c. a small quantity of carbon monoxide is evolved from the pyrogallol during absorption, and hence the results are slightly too low. After treatment with pyrogallol the gas may be passed into the cuprous chloride bulbs in order to remove any carbon monoxide that may have been formed. Usually, however, this error has no material influence on the results. Oxygen may also be absorbed by phosphorus, and this has the advantage that the presence of carbon dioxide is without influence on the result. The temperature, however, must not be below  $18^{\circ}$ , and the absorption is prevented by the presence of ammonia, olefines and other hydrocarbons, alcohol, &c.

Oxygen may also be estimated by combustion with hydrogen, either explosively by the spark or over palladium-asbestos. The hydrogen should be evolved from commercial 'pure' zinc and pure dilute sulphuric acid, or in special cases from magnesium and sulphuric acid. One-third of the contraction consequent upon combustion gives the volume of the oxygen.

**Sulphur dioxide**, by titration.

In the ordinary gases from flues, generators, &c., the constituents are estimated in the following order: Carbon dioxide, olefines and benzene, oxygen, carbon monoxide, hydrogen, methane, nitrogen (as residue or by difference).

If acid vapours are present together with one or more of the above gases the order of absorption &c. must be determined by circumstances.

#### *Apparatus and manipulation.*

**Collecting samples.** The gas to be analysed is usually drawn from the flue, chamber, &c., by aspirating it through glass tubes, which may be termed conducting tubes. When the temperature is high, porcelain tubes may be used; or if the gas has no acid properties, iron tubes can be employed. When samples are constantly taken

from the same flue &c., it is convenient to have a short piece of porcelain or iron pipe cemented into the wall and closed at the outer end with a plug, which is readily removed when the sample is taken. In cases where the gases are originally at a high temperature and possibly in a state of partial dissociation, it is important to draw the sample slowly through a somewhat long tube in order that the gas may cool slowly, since rapid cooling of the gases may leave them in a partially dissociated condition and thus lead to erroneous results.

The sample may be conveniently collected in the measuring apparatus itself; but where this is not possible, a cylindrical glass tube A, drawn out at the upper end and connected with a stopcock and capillary tube, and drawn out at the lower end and connected by caoutchouc tubing with a similar tube B, open at the top, makes a convenient sampler. The collecting tube may with advantage be provided with a stopcock at the bottom. Mr. J.E. Stead uses bottles with a tubulus at the bottom. The vessel A is completely filled with water or mercury by raising B to a higher level, and the upper stopcock is closed. The capillary tube is connected with the conducting tube, and the vessel B is lowered so that when the stopcock is slowly opened the gas is drawn into A, and the water or mercury collects in B. When A is filled the stopcocks are closed. The gas is readily transferred from A to the measuring vessel by raising B and carefully opening the stopcock.

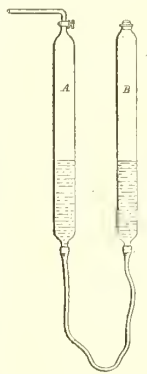


FIG. 26.

In all cases the air in the conducting tube must be expelled, and this is done by placing a T tube between the end of the tube and the collecting vessel. This T piece is connected with an aspirator, and the tube is filled with the gas before the stopcock of the collecting vessel is opened. When the collecting vessel is provided with a three-way cock, the aspirator may be connected directly with the latter. Various forms of aspirator may be used. When the volume of gas to be aspirated is small (*e.g.* in removing air

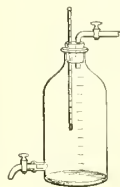


FIG. 27.



FIG. 28.

from the conducting tube), a small globular indiarubber aspirating pump is very convenient. For larger quantities of gas, glass bottles with a tubulus or stopcock at the bottom and a tube or stopcock at the top, or similar vessels of sheet zinc may be used. They are filled with water,

the upper tube being connected with the tube which passes into the flue, and the water is allowed to flow from the tap at the bottom. The volume of gas aspirated is determined by measuring the volume of water which flows from the aspirator, and correcting this volume for temperature &c. in the usual way (*v. ASPIRATOR*).

When aspiration is to be continued for a long time, one of the various forms of water pump may be used. The volume of air aspirated in a given time with a given pressure of water may be determined once for all by direct measurement, or a small gas meter may be placed between the pump and the vessel into which the gas is passed.

If the gas has to be kept for some time before analysis, or if it has to be transported from one place to another, it may be collected in glass tubes which have previously been drawn out at each end. As soon as the tubes are full the ends are closed by stoppers of indiarubber tube and glass rod, or are hermetically sealed by fusion. If the quantity of gas is large, cylindrical zinc vessels with conical ends closed by indiarubber corks answer very well.

*Estimations by titration.*—A measured quantity of the appropriate standard solution is placed in a flask or a Woulff's bottle fitted with two tubes, one of which dips into the liquid and is connected with the tube placed in the flue &c., whilst the other ends just below the cork and is connected with an aspirator. After aspiration has been continued for a sufficient length of time the excess of reagent is determined by titration. The volume of gas aspirated is determined by the volume of water which has run from the aspirator or by means of a gauge attached to the aspirator. This volume of water, however, represents a volume of gas saturated with moisture and at a temperature and pressure which must be determined by means of a thermometer attached to the aspirator and a barometer in close proximity; the volume under standard conditions is calculated in the usual way. In calculating the percentage composition of the gas it must be borne in mind that the original volume of the gas was the sum of the volumes of the absorbed constituent and the volume which has passed into the aspirator.

If  $V_1$  is the volume of the absorbed gas and  $V_2$  the volume which has passed into the aspirator, both under standard conditions, then  $\frac{100 \times V_1}{V_1 + V_2}$  = per cent. of  $V_1$  by volume.

This method may be applied in the estimation of—

**Ammonia**, by absorption in sulphuric acid and titration with alkali.

**Carbon dioxide** (in small quantities), by absorption in standard baryta solution and titration with oxalic acid.

**Chlorine**, by absorption in a standard solution of arsenious oxide in sodium carbonate, and subsequent titration with iodine after saturating with carbon dioxide.

When hydrochloric acid and chlorine occur together, the latter is determined separately in one quantity, and a second quantity is absorbed in the solution of arsenious oxide in sodium carbonate free from chlorine, and the total chlorine is determined by titration with silver

nitrate, using Volhard's thiocyanate method. In calculating the percentage composition it is important to remember that 1 vol. of chlorine produces 2 vols. of hydrochloric acid.

**Hydrochloric acid**, by absorption in sodium carbonate and titration with silver nitrate, or, in absence of carbon dioxide and other acids, by absorption in standard potash or soda, and subsequent titration with an acid.

**Hydrogen sulphide**, by absorption in standard iodine and titration with thiosulphate; or by absorption in bromine water and gravimetric estimation as barium sulphate.

**Nitrogen oxides**, by absorption in acidified permanganate solution of definite strength, the gas being passed until the solution is just decolourised. This method gives the amount of nitrogen oxides in terms of their reducing power.

**Sulphur dioxide**, by absorption in standard iodine solution and titration with thiosulphate, or by absorption in bromine water and gravimetric estimation as barium sulphate. This latter plan may be adopted when the proportion of sulphur dioxide is very small and a large volume of gas must be aspirated.

*Measuring and absorption apparatus.*—Only those forms which have come into general use and are of wide applicability will be described here. Descriptions of the numerous other modifications will be found in Winkler's *Chem. Unters. der Industrie-Gase*, Winkler and Lunge's *Technical Gas Analysis*, and in Fr.

An extremely convenient device which is applied to almost all the forms of apparatus is the three-way stopcock. This has the usual

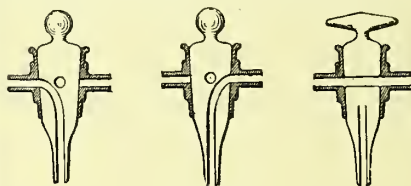


FIG. 29.

transverse bore, but the plug itself is elongated in the form of a tube, the bore of which is continued in a curved direction through the plug and opens at the side in the same plane, but in a direction at right angles to the transverse bore. By means of this tap two tubes can be made to communicate with one another, or either of them separately can be put in communication with a third tube or with the air.

*Orsat's apparatus.*—The measuring tube or burette consists of a cylindrical bulb terminating at one end in a capillary tube and at the other in a narrow tube of uniform bore graduated in tenths of a cubic centimetre. The total capacity of the tube from the zero to the capillary is 100 c.c., and the lower end of the tube is connected by caoutchouc tubing with a 'level-bottle,' the height of which can readily be adjusted. The burette is inclosed in a cylinder which is filled with water at a constant temperature. The capillary from the upper end of the measuring tube is carried horizontally along a wooden support. Other capillary tubes provided with stopcocks are fused into it at right angles and communicate

by means of very short lengths of stout indiarubber tubing with the absorption pipettes, each of which consists of a pair of somewhat large cylindrical bulbs communicating at the bottom by a curved tube. The bulbs nearest the

and the indiarubber tube is closed by a pinchcock. The level-bottle is again lowered, and by cautiously opening the pinchcock the water is allowed to descend exactly to the zero, and the pinchcock is closed. The tap at the end of the main capillary is opened for an instant so that the excess of gas may escape and the 100 c.e. remaining in the burette may be at atmospheric pressure.

In order to bring the gas into any one of the absorption bulbs, the level-bottle is raised and the tap of the particular bulb is opened. The gas passes into the bulb, and by alternately raising and lowering the level-bottle the gas can be passed backwards and forwards several times, care being taken that the absorbing liquid does not pass through the stopcock. The gas is finally drawn off so that the absorbing liquid just reaches the stopcock, the latter is closed, and after readjusting the levels the volume of gas is again read off. After making the necessary corrections, the decrease in volume is of course the volume of the gas which has been absorbed. The order in which the absorbing liquids should be applied has already been given (p. 157).

Lunge has added to this apparatus a capillary tube with palladium asbestos, connected with a bulb similar to the absorption bulbs but containing water only.

*Hempel's apparatus.*—The measuring apparatus consists of a burette, and a plain tube of the same length and diameter, which serves as a level-tube. The burette holds 100 c.e. from the zero to the capillary, is graduated in tenths of a c.e., and terminates at the top in a capillary tube to which is fitted a short piece of stout-walled caoutchouc tubing closed by a pinchcock. Both the burette and the level-tube are fixed at the bottom into heavy circular stands, and each has a side tubulus near the bottom over which is slipped the caoutchouc tube by which they are connected. It is advisable to make all the joints secure with copper wire. In order to make the measurements more accurate the burette may be surrounded by a wider tube filled with cold water (Winkler).

The pinchcock is opened and both tubes are rather more than half filled with water. The burette is completely filled with water by raising the level-tube until the water runs out of the indiarubber tube at the top, and the pinchcock is then closed. By means of the indiarubber tube the burette is attached to the conducting tube, which has already been filled with the gas, the level-tube is lowered, and the pinchcock opened. When sufficient gas has been drawn in the pinchcock is closed, the levels adjusted, and the volume read off in the usual manner. If it is desired to admit exactly 100 c.e., proceed in the same way as described under Orsat's apparatus.

The reagents are contained in *absorption pipettes*. Simple absorption pipettes consist of two bulbs which communicate at the bottom by a bent tube, one bulb being at a higher level than the other. The upper part of the lower bulb terminates in a straight capillary tube, which extends to a slightly greater height than the higher bulb and serves to connect the pipette with the burette. In the *tubulated pipette* the bottom of

capillary tubes are fitted with short lengths of glass tubing so that a large surface of the reagent may be exposed, and the other bulbs receive the liquids when they are driven out from the first bulbs by the gas. Any number of bulbs can, of course, be attached to the main capillary, and at the end of it there is a three-way tap communicating with the aspirating tube or with the air.

The burette is filled with water by placing the liquid in the level-bottle and raising the latter, and the stopcocks are then closed. The absorption bulbs are rather more than half filled with the liquid reagents and by opening the stopcocks and placing the level-bottle below the apparatus the liquids are drawn up so as to fill completely the bulbs connected with the capillaries. The stopcocks are then closed.

The burette is filled with water up to the capillary tube by raising the level-bottle, and the far end of the capillary tube is connected with the tube along which the gas is to be conducted. The lower end of the three-way tap is connected with an indiarubber aspirator, and the air is removed from the conducting tube by aspirating the gas through it. The level-bottle is then lowered, the tap is turned through 90°, and the gas is drawn into the burette. When a sufficient volume has entered, the tap is closed, the levels inside and outside the burette are adjusted by raising the level-bottle, and the volume of the gas is read off as soon as the temperature is constant. If it is desired to operate upon exactly 100 c.e., the gas is drawn in until the water is a little below the zero, the tap is closed and the level-bottle is raised so that the gas is slightly compressed and the water rises above the zero (time having been given for the liquid to run down from the sides of the burette),

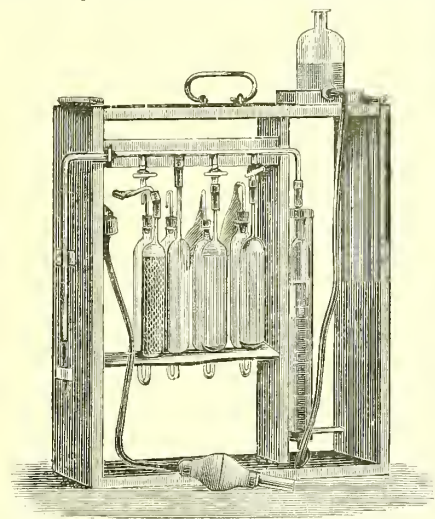


FIG. 30.



the lower bulb is provided with a tubulus, which can be closed with a caoutchouc stopper, and through which solid reagents such as phosphorus or zinc can be introduced. A *composite absorption pipette* consists of two similar pairs of bulbs, the second pair containing water or some other liquid which protects the reagent in the first from the action of the air. Composite pipettes are used with alkaline pyrogallol, cuprous chloride solution, bromine water, and similar reagents.

In making the absorptions the pipettes, which are attached to wooden stands, are placed on a table stand of such height that the top of the capillary of the pipette is level with the top of the capillary of the burette. The burette and pipette are joined by means of short pieces of caoutchouc tubing and a short piece of capillary tube bent twice at right angles. The volume of air contained in this capillary is so small that it does not introduce any appreciable error. Care is taken that the capillary of the absorption pipette is filled just up to the top with the reagent. The connections being made, the level-tube, which should be full of water, is placed on the table stand and the pinchcock is opened. The gas passes into the pipette, and by raising and lowering the level-tube the whole of the gas can be passed backwards and forwards two or three times; or the gas may be allowed to remain in contact with the liquid in the pipette. When absorption is complete, the level-tube is lowered until the reagent is drawn just up to the top of the capillary of the pipette, the pinchcock is closed, and a second reading is taken.

When combustions have to be made, the capillary tube containing palladium asbestos is inserted between the burette and a simple absorption pipette containing water only.

When gases very soluble in water have to be measured, a burette is used, provided at the top with an ordinary stopcock and at the bottom with a three-way stopcock, the volume between them being exactly 100 c.c. The burette must be perfectly dry before being filled, an end which is most quickly effected by rinsing the burette with water, then with alcohol, and finally with ether, and passing a current of warm air through it. The lower end of the burette is connected with the conducting tube by means of the three-way tap, the other end is connected with an aspirator, and a current of the gas is drawn through the burette until the air is completely expelled. The stopcocks are then closed, care being taken that the gas in the tube is at atmospheric pressure. The absorptions &c. are made in the same way as with the ordinary burette.

*Elliott's apparatus* (C. N. 44, 289) consists of a burette, *B*, terminating in a capillary tube bent at right angles and fitted with a stopcock, *c*, and an absorbing tube, *A*, of the same length and diameter, terminating at the top in a three-way capillary tube, the horizontal part of which is connected with the capillary of the burette, whilst the vertical part is fitted with a stopcock, *r*. The end of this vertical part is carefully ground, and over it fits a small cylindrical funnel, *M*, to contain the absorbing reagent. The bottoms of both the burette and the absorbing tube are closed by caoutchouc stoppers and connected with

level-bottles, *K*, *L*, by means of caoutchouc tubing, a three-way glass stopcock being inserted between the absorbing tube and its level-bottle. The accuracy of the measurements is increased by inclosing the measuring tube in a water-jacket. In the original apparatus explosions

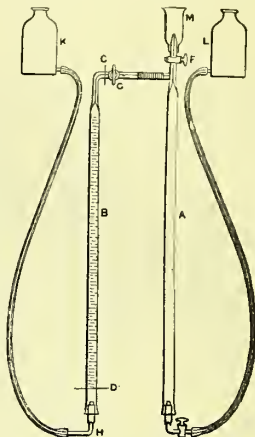


FIG. 31.—ELLIOTT'S APPARATUS FOR GAS ANALYSIS.

were made in a separate tube similar to the absorbing tube, but with platinum wires and without the stopcock and funnel. Either the measuring tube or the absorption tube may, however, be provided with platinum wires, and the two tubes may be connected by fusion instead of by caoutchouc tubing.

The tubes may be used either with water or with mercury, and are filled with liquid and afterwards with gas in much the same way as Hempel's burette, the gas being drawn into the absorbing tube through the three-way tap at the bottom and passed over into the measuring tube. Absorbing reagents are placed in the cup over the absorbing tube, and after the measured volume of gas has been passed into the tube and the burette stopcock closed, the level-bottle is lowered and the reagent drawn into the tube by cautiously turning the funnel stopcock, care being taken that no air is drawn in at the same time. When absorption is complete the gas is transferred to the burette, and the reagent is afterwards driven up into the funnel and the tube rinsed out with water introduced through the funnel and then driven back by raising the level-bottle. A second reagent may be introduced and a second absorption made.

Mr. J. E. Stead has devised a form of apparatus which is convenient for the analysis of furnace gases, but is not applicable for general purposes.

The *nitrometer*, originally devised by Lunge (B. 11, 436) for the estimation of nitrogen oxides in oil of vitriol, is capable of being applied to gas analysis and a large number of other determinations. It consists (Fig. 32) of a burette, fitted at the top with a three-way tap and a cup-shaped funnel, and communicating at the bottom by means of caoutchouc tubing with a plain tube of the same diameter, which serves as a level-tube. When large quantities of gas have

to be measured, the upper part of the burette is expanded into a bulb, and there is a similar bulb on the level-tube (Fig. 33).

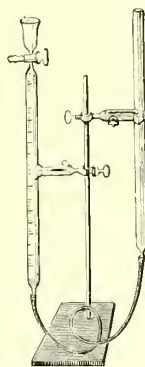


FIG. 32.

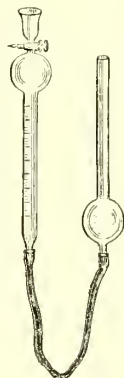


FIG. 33.

This apparatus is used with mercury, and is thus suitable for the analysis of gases soluble in water. It can be used in the same way as Hempel's burette, and for all purposes to which the latter is applicable. It may also be used without absorption pipettes, the reagent being introduced by means of the cup in the manner described under Elliott's apparatus, but since the reagents cannot be removed without removing the gas, this latter method is only applicable when the reagents do not interfere with each other—e.g. for the absorption of carbon dioxide by potash, followed by the absorption of oxygen by potash and pyrogallol.

The estimation of nitrogen oxides in solution in sulphuric acid is conducted in the following manner. The apparatus is filled with mercury, so that when the tap is open between the burette and the cup, and the level tube is raised, the mercury just passes through the tap and stands at a height of about 2 inches in the level-tube. The tap is then closed and 0.5 to 5 c.c. of the sulphuric acid, according to the quantity of nitrogen oxides which it contains,<sup>1</sup> is placed in the cup, the level-tube is lowered, and the tap is turned so that the acid is nearly all drawn into the burette without any air being admitted. The cup is rinsed with two successive quantities of 2 to 3 c.c. of pure acid, which is drawn into the cup with the same precaution as before. The tap being closed, the burette is taken out of the clamp and agitated in such a manner that the liquid is brought thoroughly in contact with the first 10 cm. or so of the mercury, which is broken up into bubbles. Nitric oxide is formed and collects in the upper part of the tube. When no more gas is given off, the levels are adjusted and the volume read off after the froth has subsided. In adjusting the levels the difference between the specific gravity of the acid and the mercury is allowed for by taking 6.5 mm. of acid = 1 mm. of mercury. Place a small quantity of acid in the cup and open the tap; if the acid is drawn in the pressure in the burette was

too low, if gas escapes the pressure was too high. It is better to err on the side of too low pressure, which is readily corrected by allowing acid to run in from the cup and taking another reading.

In agitating, care should be taken that the drop of acid which collects in the top of the burette just below the tap does not escape contact with the mercury, otherwise the results will be too low.

To prepare for another estimation, the level-tube is raised and the tap is opened so that all the acid and some of the mercury is driven into the cup, and the tap is then turned so that the acid runs out at the side.

The nitrometer may be used for the valuation of nitrites and nitrates, which are introduced in the form of a concentrated aqueous solution, care being taken that the proportion of water to acid does not exceed 2 parts of aqueous solution to 3 parts of the strongest acid. It may also be used for the estimation of nitrates and nitrites in potable waters, and in fact for almost any determinations in which a definite volume of gas is given off. For example, the estimation of carbonic acid; of urea by hypobromite (the reading being increased by 9 p.c. to correct for solubility of the gas and incomplete decomposition); hydrogen peroxide by an acidified solution of potassium permanganate, or *vice versa*, the value of a permanganate solution by means of hydrogen peroxide, &c. (See Lunge, B. 11, 436; C. S. I. 4, 447, and 5, 82; Fr. 25, 309; and the translation of Winkler's Technical Gas Analysis (1885); also Allen, S. C. I. 4, 178.)

**Calibration of Instruments.**—All the gas burettes described may be calibrated in much the same way as an ordinary burette (*v. Volumetric Methods*), by filling with water or mercury, and drawing off aliquot portions and weighing them, the temperature of the liquid being noted and the proper correction made for expansion. If any error is found it must be used as a correction in subsequent readings. C. H. B.

**ANAMIRTA COCCULUS** or **A. PANICULATA** (botanical name of *Cocculus indicus*. Grains of Paradise) *v. COCCULUS INDICUS*.

**ANANAS, OIL or ESSENCE OF.** A solution of ethyl butyrate in 8 to 10 times its weight of alcohol. It possesses the odour of the pine-apple (*Ananassa sativa*), and is employed in confectionery and perfumery; also to imitate the flavour of rum (Hofmann, A. 81, 87).

**ANANDONIS GREEN, Hydrated chromium sesquioxide, v. CHROMIUM.**

**ANATASE.** A nearly pure oxide of titanium  $TiO_2$ , found most abundantly at Bourg d'Oisans in Dauphiné; and, together with Brookite, in North Wales.

**ANCHIETA BARK.** The root bark of *Anchietea salutaris*, one of the Violaceæ, a bushy shrub growing at Rio de Janeiro. It contains anchietine, a substance crystallising in straw-coloured needles, having a nauseous taste. Used for syphilis and quinsy (Peckolt, Ar. Ph. [2] 97, 271).

**ANDA-ASSU, OIL OF.** An oil obtained from the seeds of *Joannesia princeps*, belonging to the Euphorbiaceæ, growing in Brazil. It is clear, slightly yellowish, odourless, with a taste at first nauseating and then saccharine. It solidifies at  $8^\circ C$ , its sp.gr. at  $18^\circ C$  is 0.9176 (Ph. [3] 12, 380).

<sup>1</sup> To avoid measuring out such small quantities as 0.5 c.c., the highly nitrated acid should be diluted with a definite volume of pure concentrated acid, and 5 c.c. of this solution taken for the estimation.

**ANDAQUIES WAX.** The wax of a peculiar species of bee found near the Orinoco and Amazon rivers, and used as a substitute for ordinary beeswax in the manufacture of candles &c. Its density is 0.917; it melts at 77°C.; it contains 50 p.c. palu wax, 45 p.c. cerosine, and 5 p.c. of an oily fat of undetermined composition (Lewy, A. Ch. [3] 13, 458) v. Wax.

**ANDREWSITE.** A mineral from Phoenix Mine, Liskeard, of a dark-green colour. Hardness = 4, sp.gr. 3.475.

$\text{Fe}_2\text{O}_3$   $\text{Al}_2\text{O}_3$   $\text{FeO}$   $\text{CuO}$   $\text{P}_2\text{O}_5$   $\text{H}_2\text{O}$   $\text{MnO}$   $\text{CaO}$   
44.64 0.92 7.11 10.86 26.09 8.79 0.60 0.39

$\text{SiO}_2$

0.49 = 99.59.

**ANDROPOGON OILS.** *Rosé* or *Roshé* Oil, *Oil of Rose Geranium*, *Ginger Grass* Oil, or *Turkish Geranium* Oil, is obtained from *Andropogon Nardus* and other species, a grass growing in the East Indies, Persia, and Arabia. It is a yellowish thin liquid, having an agreeable aromatic odour; it does not solidify readily. Treated with an equal bulk of concentrated sulphuric acid it acquires a strong fatty odour; it turns dark-yellow when exposed to the vapour of nitric peroxide (Ph. [3] 10, 24).

Citronella oil is prepared from *Andropogon Schranthus*, it boils at 200° and has a sp.gr. of 0.8741 at 20°.

Lemon grass oil is made from *A. Nardus*, and Indian geranium oil from *A. muricatus*.

**ANDROGRAPHIS PANICULATA** or *Karyat*. An Indian plant; is used as a tonic, and is similar to quassia in its action.

**ANETHUM GRAVEOLENS.** The common Dill, cultivated in England and the South of Europe. Has a hot sweetish taste and is used in medicine and for flavouring spirituous cordials.

**ANGELICA.** (*Angelique*, Fr.; *Anglika*, Ger.) The *Angelica archangelica*, an aromatic unbelliferous plant, indigenous to the north of Europe. A candy is made from its stems, stalks, and midribs. The essential oils of the roots and seeds are used in the preparation of gin and of aromatic bitters.

*Angelica balsam* is prepared by extracting the roots with strong alcohol, evaporating, washing the residue with water, and extracting with ether. It is of a black-brown colour and contains angelica oil, angelica wax, and *angelicin*  $\text{C}_{15}\text{H}_{20}\text{O}$  (Buchner, A. 42, 226), a crystallisable substance melting at 126°-5 C. (Brunner, N.R.P. 24, 641; C. J. 29, 939).

The essential oil of the root contains  $\beta$ -terangelene  $\text{C}_{10}\text{H}_{16}$ , b.p. 166°.  $[\alpha]_D^{20} = 5.39'$ , sp.gr. 0.870 (Naudin, C. R. 93, 1446; 96, 1152; J. 36, 1423; Bl. [2] 39, 114). Beilstein a. Wiegand found in the oil four terpenes, having the following boiling-points and specific gravities:

	b. p.	sp.gr.
a	158°	0.8609 at 16°-5
b	171-175	0.8504 at 16°-5
c	176°	0.8481 at 16°-5
d	250°	

(B. 15, 1,741; C. J. 42, 1,300).

The essential oil of the seeds contains methyl-acetic acid, hydroxymyristic acid and terebangelene  $\text{C}_{10}\text{H}_{16}$ , b.p. 172°-5, sp.gr. 0.833 at 0°C.  $[\alpha]_D^{20}$  200 mm. +26°16' (Naudin, C. R. 93, 1146 C. J. 42, 410; Müller, B. 14, 2476; C. J. 42, 469).

**ANGICO RESIN.** A Brazilian gum obtained from *Acacia angico*; soluble in water and proof spirit. Used in chest complaints (Symes, Ph. 3, 13, 213).

**ANGLESITE.** Native lead sulphate, first found at Dary's mine, Anglesea.

**ANGOSTURA BARK** or **ANGUSTURA BARK** v. **CUSPARIA BARK**.

**ANHYDRITE** v. **CALCIUM**.

**ANIL.** The name of the American species of the indigo plant, *Indigofera anil*.

Formerly also used as a synonym for indigo, and latterly as a synonym for phenylimide.

**ANILINE.**

*History.*—First observed by Unverdorben in 1826 among the products of the destructive distillation of indigo. Detected by Runge in coal tar in 1834, and by Fritzsche in 1840 among the products obtained by distilling indigo with caustic alkalis. Prepared by Zinin in 1840, by the reduction of Mitscherlich's nitrobenzene with sulphuretted hydrogen. Unverdorben called his product *krystallin*; Runge, kyanol; Fritzsche, anilin; Zinin, benzidam.

In 1843 Hofmann showed that nitrobenzene could be reduced by a metal such as zinc in the presence of a dilute acid, and also that *krystallin*, kyanol, anilin, and benzidam, were identical with each other. Shortly afterwards Béchamp stated that nitrobenzene could be reduced by ferrous acetate in the presence of water, but that the oxalate, sulphate, &c., had no effect.

In the year 1856 Perkin's discovery of mauve gave rise to a commercial demand for aniline, and the manufacture was commenced by Messrs. Simpson & Maule.

*Preparation.*—Benzene, then only obtained in small quantities and with much difficulty, as the treatment of tar scarcely existed, was introduced into glass balloons (known as 'bolt heads') of 1 gallon capacity, and the calculated quantity of nitric acid, mixed with about an equal volume of oil of vitriol, was gradually added, the mixture swung round and well agitated, and then allowed to stand. It was usual to have about twenty balloons in a row, and to add acid in turn until the reaction was complete.

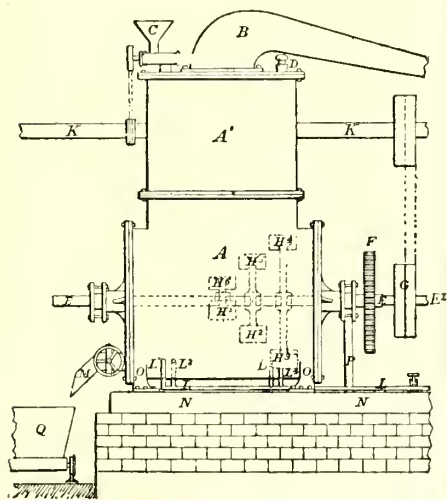
The nitrobenzene was separated, washed, and reduced with iron borings and acetic acid, at first in a copper still, later in an iron cylinder. The aniline was freed from water, rectified, and was then ready for use. The selling price was about a guinea a pound.

Somewhat later cast-iron cylinders of considerable size were used for the reduction, acetic acid being still used and neutralised with soda or lime at the end of the reaction, and the aniline was in some factories distilled off over a naked fire, in others steam was blown into the mixture, and the aniline and water condensed and separated. Acetic acid continued to be used until about 1866.

In that year Messrs. Simpson, Maule, & Nicholson removed their works to Hackney Wick, where the manufacture was carried out on a very large scale, the apparatus, which has undergone little change since, consisting of horizontal stills furnished with powerful agitators, and the treatment consisting in reduction mainly by the use of iron and water, hydrochloric acid being employed to start the reaction.



The stills consist of a cast-iron **T** piece 5 feet in diameter and 6 feet long; this is bolted to a cast-iron bed-frame with the leg of the **T** turned upwards, and the two ends closed with circular plates furnished with stuffing boxes through which a heavy steel spindle passes. To the spindle curved cast-iron arms



DESCRIPTION OF HORIZONTAL ANILINE STILL.

- A. Still body cast as a **T** in one piece. The ends closed by plates bolted on to flanges.
- A'. Upper portion bolted to the body top, closed by top plate bolted on.
- B. Head.
- C. Apparatus for continuous introduction of swarf.
- D. Wooden plug closing orifice through which the nitrobenzene is introduced.
- E E. Steel spindle to which agitators are keyed. It passes through stuffing boxes cast on end plates.
- F'. Counter shaft.
- F. Driving wheel gearing into pinion on countershaft to the rear.
- G. Fast and loose pulleys on countershaft.
- H, H, H'. Advancing arms of agitators.
- H', H', H'. Retreating arms of agitators.
- K K. Main shaft carrying drums to drive C and G by means of belts.
- L. Steam pipe.
- L, L, L, L. The four branches of steam pipe entering still at bottom, two on each side.
- M. Sludge valve and shoot.
- N N. Cast-iron foundation frame.
- O O. Brackets cast on still body holding it down to frame.
- P. One of the standards carrying plunger blocks for countershaft.
- Q. Sludge truck on tramway.

For the sake of clearness only three of the agitators are shown, and for the same reason two bolts only are shown to each flange, top and end plate, to the glands and stuffing boxes, the head, &c.

are keyed in a series arranged to form a helix. The arms are furnished at the ends with cast-steel shoes or scrapers which are so adjusted as just to scrape the inside of the still body. The third arm of the **T** piece projects upwards and is prolonged by a cylinder of cast-iron 4 feet deep, bolted on to a flange cast on the body. The top of the still is closed with a circular iron plate, from the centre of which a cast-iron head 24 inches in diameter, diminishing to 4 inches, serves to carry off the

steam and aniline vapour to the condenser. Round the head are arranged a manhole and two 4-inch circular apertures for introducing the iron. In the latest form of still a **T** tube fitted with a wide hopper and carrying a worm is bolted on to one of the 4-inch openings. By means of this arrangement the iron is brought into the still in a continuous stream. Into the bottom of the still four branches of a steam pipe are fixed. In one end a 4- or 6-inch opening closed with a bonnet and lever, or a large screw valve, serves to discharge the residues into iron trucks run underneath the orifice. To the end of the spindle a cog-wheel gearing into a spur-wheel is fixed by which the agitator is rotated. In some cases a small engine is used to drive the agitators directly.

The head delivers the vapours directly into a 4-inch tube communicating with a multitubular condenser consisting of about 400  $\frac{1}{2}$ -inch brass tubes each 6 feet long, surrounded by water delivered at the lower end of the condenser jacket which is 6 feet deep. The hot water flows off at the upper end in the usual manner.

The iron used for reduction is that technically called 'swarf;' it consists of the scrapings of soft castings. Before use it is passed through a coarse sieve to remove pieces of iron, bolts, nuts, &c., which have found their way into it, and it is then ground under heavy granite edge runners until it will pass easily through a 'twenty hole sieve' (twenty holes to the inch linear = 400 to the square inch).

It is to be particularly noted that hard cast borings or turnings and wrought-iron borings and turnings are quite unsuited for reducing purposes, though in the more violent reaction consequent on the reduction of metadinitrobenzene, about 25 p.c. of coarse swarf may be mixed with the ground swarf with advantage.

All being ready a portion of the iron is introduced into the still through one of the 4-inch openings, which is then closed with a wooden plug (this serves as a rough safety valve), together with some water. Steam is blown in, the acid next run rapidly in from a carboy, and the nitrobenzene which has been weighed out into a cast-iron tank allowed to steadily flow in.

The reaction begins immediately and a copious distillate of water, aniline, and nitrobenzene flows from the condenser, and is continuously returned to the still by an elevator. The worm apparatus is now started and the main body of the ground iron steadily poured into the still. The distillate, examined from time to time by the foreman, shows a steadily increasing solubility on addition of muriatic acid and considerable dilution, and at length after about six to eight hours no traces of nitrobenzene remain. Care must be taken to control the delivery of iron, as, if the reaction becomes very violent, benzene and ammonia may be produced and serious loss incurred.

The steam, which had been checked while the action was vigorous, is now turned on, and a diverting tube slipped over the condenser nozzle directs the distillate into a sunk tank, from which a steam pump throws it into square wrought-iron tanks with dished bottoms, supplied with draw-off cocks in the bottoms and sides.

The Continental practice differs slightly in various details from that above described, the

still in use being vertical cylinders with vertical agitating arrangements. The charges of nitrobenzene in use are smaller and the proportions of iron and acid used are relatively larger.

The charge for the still just described is:

Ground swarf	. . .	2,688 lbs.
Nitrobenzene	. . .	2,350 "
Muriatic acid	. . .	116 "

The usual Continental charge is:

Ground swarf	. . .	660 to 720 kilos.
Nitrobenzene	. . .	600 "
Muriatic acid	. . .	60 "

It was formerly the custom to make the contents of the still alkaline with soda or lime at the end of the reaction. In this country that method has long been abandoned, the acid in the presence of so great an excess of iron not retaining a trace of aniline, the still liquors consisting only of a very dilute solution of ferrous chloride, and the main bulk of the iron escaping as 'black stuff,' i.e. magnetic oxide of iron  $\text{Fe}_3\text{O}_4$  mixed with a little unaltered metal.

The aniline and water remain at rest in the settling tanks for twenty-four to forty-eight hours or longer, when the lower layer of aniline is drawn off and sent to the rectifying still. The water, technically known as 'liquors,' goes to the boiler which serves to supply steam to the aniline stills. Where more than one kind of aniline is made it is therefore necessary to have separate boilers for each for this purpose.

The solubility of water in aniline varies between 2 and 5 p.c. according to the temperature of the liquors.

Aniline dissolves about 5 p.e. of water, nearly the whole of which is expelled on rectification, which is carried out in wrought or cast-iron pot stills of various forms and sizes. The water comes off with the first 10 to 15 p.c. of the distillate. A small quantity, however, remains obstinately attached to the aniline, and can only be removed by prolonged digestion over powdered soda or potash.

Good commercial rectified aniline should not contain more than  $\frac{1}{2}$  p.c. of water.

The process of reduction and rectification as described applies to all the various qualities of 'aniline oil' now recognised. These are 'pure aniline oil,' 'aniline for red,' and 'toluidine,' which occurs as a more or less crude orthotoluidine containing 25 p.c. to 35 p.c. of paratoluidine. Modifications of the process are also in use for the production of xylydine and alpha-naphthylamine, and of the reduction portion for the manufacture of metaphenylene- and metatolylene-diamine from the respective dinitro-compounds.

The demand for xylydine caused by the production of the azo-scarlets, in the manufacture of which it was largely used, has had a very great effect on the manufacture of anilines. Formerly a considerable quantity of xylene was left in the so-called '30/90 benzol' from which aniline for red was usually made, the rest of the mixture consisting of toluene and benzene. Pure toluene was not made, and pure benzene only to a very limited extent. The so-called pure aniline was also extremely impure owing to the very defective purification of the benzene used for it.

Now, however, the Savalle still has been brought to a great perfection, and in consequence benzene boiling 99.9 p.c. within half a degree is easily obtainable, as are also pure toluene and xylene. It is therefore customary with aniline makers to make aniline from pure benzene and also from what is now termed '25 p.c. benzene,' the other 75 p.c. consisting of toluene only. The crude aniline for red obtained from it contains roughly 25 p.c. aniline, 20 to 25 paratoluidine and 45 to 50 orthotoluidine. From the toluene crude toluidine is also made.

As it is now customary with all makers of magenta to use aniline of specified gravity, the aniline maker adjusts his aniline for red by the addition to it of pure aniline or crude toluidine according as he wishes to raise or depress the gravity.

The specific gravity of the aniline for red as obtained at first being at 15°C., about 1.0060 to 1.0065 as compared with water at the same temperature, and pure aniline having under the same conditions a gravity of 1.0268 and toluidine from 1.0010 to 0.9987, it is readily seen how a simple calculation indicates the amount of pure aniline to be added to bring the gravity to 1.0075, or to any other of those in use in different factories. It is generally held that the rosaniline base intended for the manufacture of blue is better suited to that purpose when obtained from high gravity aniline, whereas for the preparation of magenta crystals, low gravity aniline is recommended by its greater cheapness.

Besides the above anilines, factories have to deal with a variety of others occurring as by-products in the various manufactures. Thus in the magenta process, when arsenic acid is used, upwards of one-fourth of the aniline distills off from the melt still, together with a considerable quantity of water or liquors. This aniline is found on rectification to have a much higher gravity (1.0150 to 1.0090), to be proportionately richer in true aniline and orthotoluidine, and practically free from paratoluidine. The treatment of this varies greatly in different factories. Formerly it was used for producing very red shades of blue, now it is very often returned to the red melt still, as portion of a subsequent charge, or else used up in the manufacture of saffranine, or crude paratoluidine may be added to it to restore it to a fit state for the magenta manufacture.

In the manufacture of magenta by the nitrobenzene process, mixtures of aniline with small quantities of nitrobenzene are also recovered and have to be similarly applied to useful purposes.

The pure aniline used in phenylation of rosaniline base is also in part recovered and rectified for subsequent use.

In like manner, the preparation of mono- and di-methyl and mono- and di-ethyl aniline is accompanied with the recovery of various partially methylated or ethylated anilines in small quantities; these as a rule find their way into the red melt.

Liquors in excess of what is required for the aniline boilers may be deprived of most of their aniline by a saturation with common salt and separation and rectification of the supernatant aniline.

*Valuation of Commercial Aniline Oil.*

Pure aniline, as it occurs in commerce, contains as impurities traces of insoluble hydrocarbons and of orthotoluidine, sometimes traces of sulphuretted hydrogen, and if carelessly made, of nitrobenzene, benzene, and ammonia. Besides these, which should be carefully tested for, there is possibly a certain amount of amidothiophen which has no deleterious action for most if not all of the purposes for which aniline is used, and which, moreover, for the present at least cannot readily be got rid of.

The method of testing usually adopted is to determine the boiling points of the sample. For this purpose most chemists are in the habit of taking 100 c.c., introducing it into a small boiling flask with side tube, and distilling it through a short condenser into a graduated 100 c.c. cylinder. Readings of the thermometer are taken as each 10 c.c. of the cylinder fills, and the last when 95 c.c. are filled. It is also usual to note the temperature when the first drop has fallen from the condenser. The thermometer readings should be corrected for barometer and immersion of mercurial column in the vapour of the liquid, and of course for the errors peculiar to the thermometer in use.

In the writer's opinion 100 c.c. is too small a quantity for this test, and his own practice of many years has been to use 250 c.c., reading as usual by tenths of the distillate over. The first drop reading may also be neglected, but on the other hand it is exceedingly useful to skilfully drive the flask to dryness and get the temperature as the last drop disappears from the bottom of the flask. A few fragments of platinum wire, fire-brick, or wrought iron, should be placed on the bottom of the flask and great care used to adjust the size of the flame and rate of boiling. The flask also should be held by the neck in a good clip over the naked flame, gauze being apt to cause currents of heated gas to blow up round the neck of the flask and superheat the vapour.

The specific gravity of the sample may also be taken, as is usual with aniline for red, although this indication is not of great moment if the boiling-points are good.

The following are three samples of pure aniline from the writer's note-book:—

Per cent. over	No. I.	No. II.	No. III.
10	184.7	184.6	184.6
20	184.7	184.8	184.6
30	184.7	184.8	184.7
40	184.7	184.8	184.7
50	184.8	184.8	184.8
60	184.9	184.8	184.8
70	185.0	184.8	184.9
80	185.1	184.8	184.9
90	185.1	184.8	185.0
	186.7 Dry	186.8 Dry	

Sp.gr. at 15°	1.02710	1.02684	1.02690
comp. with water at 15°			

Pure aniline may be tested for insoluble oils by dissolving 10 c.c. in an equal volume of hydrochloric acid and diluting with water to 100 or 150 c.c. The best samples show a slight opalescence under this treatment, and the smell of the 'light stuff,' as the insoluble oils are called, is always distinguishable. These accu-

mulate in the recovered anilines from various processes, as they are inert, while the bases are consumed in the reactions they take part in. The trace of toluidine only shows itself when a considerable quantity of commercial pure aniline is made into acetanilide. On recrystallising this and working up the mother liquors, a small quantity of impure acetyl compound of low melting-point will always be found in the most soluble portion or first mother liquors.

Nitrobenzene shows itself with the insoluble hydrocarbons. A very delicate test for it is to shake the sample of aniline violently for a few minutes and then to notice the colour of the froth. The merest trace of nitrobenzene colours it a very distinct yellow.

*Aniline for Red.* This, as originally made, contained aniline, *o*- and *p*-toluidine, and xylenes. The latter are now practically never present. It is valued by its specific gravity, which is, as before stated, adjusted to suit the convenience of each user. It generally contains rather more insoluble oil than does pure aniline, and can be tested for it in the same way.

The value of the aniline for red for making the magenta melt depends on the presence of aniline together with ortho- and para-toluidine, and in good samples the proportions should not vary greatly from the following: Aniline 35.42 p.c., *o*-toluidine 35.50 p.c., *p*-toluidine 14.24 p.c. The estimation of the three bases is exceedingly difficult, in fact no satisfactory method yet exists. Titration with oxalic acid in ethereal solution of an oil, in which the proportion of aniline has been approximately ascertained by calculation from the gravity or by distillation points, is one method, now however practically obsolete. The oxalates of aniline and *p*-toluidine were precipitated as insoluble salts, and from the oxalic acid used their amount could be calculated and the orthotoluidine found.

Merz and Weith (B. Z. 433) found that if the mixed bases were converted into acetyl compounds and these dissolved in four times their weight of glacial acetic acid, and then the whole dissolved in 80 times the weight of boiling water, the whole of the *p*-acetoluide crystallised out and left the acetanilide and *o*-acetoluide in solution. P. Schoop (C. Z. 1885, 1785; S. C. I. 5, 178) has founded upon this reaction an elaborate method of calculating the composition. His method is based on an estimation of the *p*-toluidine by the Merz and Weith process, followed by a calculation of the amount of the other two bases from the specific gravity of the original sample. The results obtained are, however, very unsatisfactory, and the process has been severely criticised by C. Häussermann (C. Z. 1887, 1,223). The writer also found it to be useless. No process at present published is capable of giving even moderately correct results.

**Toluidine** liquid should boil at 197°-8°, show a sp.gr. of about 1.000, and contain 30-40 p.c. para-, the rest ortho-toluidine.

**Orthotoluidine.** The gravity of commercial orthotoluidine should be about 1.0037; boiling points about 197°-198°; should not solidify on cooling to -4°, though most samples contain enough paratoluidine to begin to show a few



crystals at this temperature. Lunge (Chem. Ind. 8, 74) has published a very elaborate and valuable table of the gravities of mixtures of *o*- and *p*-toluidine.

**Paratoluidine.** Melting-point of commercial paratoluidine 43°–45°, boiling points between 196°–198°. Crystals should be white and dry.

R. J. F.

**ANILINE BLACK.** The production of a very dark blue shade on cotton by immersing it in a solution of a chlorate and hydrochloride of aniline dates back to the year 1860, when Wilm described such a method. In the same year Calvert, Lowe, and Clift took out a patent for an identical reaction to be applied as a printing method on cotton fabrics, but stated that the colour produced was dark-green. They printed a mixture of starch paste, potassium chlorate, and aniline chloride on to the stuff, which was then passed through a weak soap solution. The dyeing substance was obtained as a separate body by the action of ferric chloride on aniline nitrate and was investigated by E. Kopp.

The first true black was patented by John Lightfoot in 1863. He directed that

50	parts of aniline
50	“ “ muriatic acid
25	“ “ potassium chlorate
50	“ “ cupric chloride solution, sp.gr. 1.440
25	“ “ sal ammoniac
12	“ “ acetic acid

should be mixed with 1,000 parts of a starch paste made by boiling 1 part of starch with from 7 to 9 parts of water.

This mixture was printed in the usual way on cotton cloth, which was then ‘aged’ by being suspended in a chamber kept at a temperature of about 86°F. (30°C.) for 48–72 hours. The pattern had then become dark-green, and the cloth was forthwith passed through an alkaline bath, when an intense blue-black was immediately developed.

The colour was so cheap, good, and fast to both light and scouring, that the process came into immediate use, and was subjected to much investigation with the object of improving it by obviating its powerfully corrosive action on the copper rollers and steel doctors of the printing machine, varying the shade, &c.; and as usual, it is needless to say, of evading the patent.

Thus Cordillot in 1863 substituted ammonium ferriyanide for the copper salt,<sup>1</sup> but the results were inferior to Lightfoot's. Lauth in 1864 substituted copper sulphide for the chloride, and much diminished the corrosive action, and C. Köchlin replaced the hydrochloric by tartaric acid with a similar result.

Later, about 1868, Lightfoot, Pinkney, and finally in 1876, Guyard, worked at the use of ammonium vanadate in place of the copper salt, the latter pointing out that 1 part of the vanadium compound was capable of converting 1,000 parts of aniline chloride into black, whilst later Witz showed that this remarkable reaction would occur, if only a few days were allowed and the temperature was that of an ordinary summer, between 1 part of vanadium salt and

200,000 parts of aniline chloride, 1 part of vanadium being as efficient as 4,666 parts of copper.

The use of ammonium vanadate rapidly spread, and large quantities of minerals were worked up in order to obtain the necessary vanadic acid, the price of the ammonium salt falling steadily until it reached a price of about twenty shillings per pound. Of late years, however, there has been a return to the older copper methods, the sulphocyanide being now in considerable favour. This change was due to the fact that ‘vanadium’ blacks were found not to stand washing as well as those produced by the copper process, repeated treatment with soap turning them from blue-blacks to green-blacks, which latter are not in favour, as they look rusty and dull. Some printers also say that vanadium black weakens, or, as it is called, ‘tenders’ the cloth, though some who have found this still continue to use the process for very fine lines.

Every detail of the process has been varied in every possible way, the number of receipts to be found in print being in fact almost innumerable.

In addition to vanadium compounds, chromium, tungsten, and cerium preparations have been used on a considerable scale.

The consumption of aniline for this purpose is very large. It is a well-ascertained fact that pure aniline gives an extremely blue black, while ortho- and para-toluidine produce impure reddish or brownish shades. The object of the printer is therefore to obtain aniline which shall exactly produce the desired shade of black, chemically pure aniline, now readily obtainable, giving too blue a shade.

In order to obviate too great an acidity in the mixture, it is also customary to employ an ‘aniline salt’ (i.e. aniline hydrochloride) as free as possible from free acid. In many works this is attained by the simple expedient of using free aniline as well as the salt, in a solution of which latter the aniline is pretty freely soluble.

The requirements of the printer are in general: 1. A well-crystallised colourless aniline salt, dry, and free from excess of acid and free from sand or grit; 2. aniline nearly free from toluidine, boiling (uncor.) 90 p.c. between 180° and 185°, and of sp. gr. about 1.023.

Aniline black can be dyed on wool by suitable modifications of the process. For instance, if a bath is prepared of

80	parts of aniline salt
40	“ “ potassium or sodium chlorate
5	“ “ muriatic acid
0.1	“ “ ammonium vanadate
1000	“ “ water

raised to boiling and the wool introduced well wrung out or centrifugated, aged by hanging in a warm room and then passed through a bath of sodium or potassium bichromate, a good permanent black is developed.

The black compound which is produced in the fibre in all these processes is known as nigraniline, and may be prepared by mixing solutions of aniline salt, copper sulphate, potassium chlorate and sal ammoniac, and gentle heating. When freed from by-products by treatment with suitable solvents, it appears as a dark greenish amorphous powder, insoluble in nearly all liquids but sulphuric acid, by careful treatment with which it is converted into a sulphonic acid,

<sup>1</sup> In this and other cases where no copper salt was used the copper rollers no doubt provided enough metal, though, of, course with disastrous effects to themselves.

which, however, is of no commercial value. Heated with tin and hydrochloric acid it undergoes reduction and splits up into paraphenylenediamine and diamidodiphenylamine, a mode of decomposition which points to its relations to the saffranine group of colours. (For an account of other deep blues and greens which have of late years been sometimes sold as 'black aniline,' 'soluble aniline black,' &c., *v.* the articles on INDULINE, NIGROSINE, NAPHTHOL BLACK.) R. J. P.

**ANILINE BLUE.** One of the earliest known tests for the presence of aniline was the production of a transient blue colouration in the suspected fluid, on the addition of solution of bleaching powder. This reaction was the origin of the obsolete names of aniline, *viz.* *kyanol*, from Gr. *kyanos*, a 'blue substance' or the 'blue cornflower.'

The first aniline blue of commercial value was, however, that described in a patent taken out in January 1861, by C. Girard and G. de Laire, for heating the acetate, sulphate, oxalate, hydrochloride, arsenate, &c. of rosaniline with aniline for 5 or 6 hours. Violet-blue dyestuffs were thus obtained, and were at the time introduced into commerce by dissolving the whole melt in alcohol; the redder shade of this colour was known as 'violet imperial,' and the bluer as 'blue de Lyon.'

As a matter of fact, Messrs. Simpson, Maule, & Nicholson had produced the violet or 'purple' colour before Messrs. Girard & de Laire, but had not pushed the reaction far enough to discover the blue, and had not patented their process. During the next few years the process was the subject of a number of patents now only of historical interest, and in consequence of the discovery that the salts of rosaniline with organic acids were alone capable of undergoing phenylation in this manner, the methods of work speedily settled down into two main processes.

One of these consisted in heating rosaniline hydrochloride with aniline and fused sodium acetate, whereby acetate of rosaniline was formed with separation of sodium chloride. The heating was continued until the desired amount of phenylation, as indicated by the blueness of the melt, was attained. The melt was run out into dilute hydrochloric acid and boiled, thrown on a filter and washed, and after drying the colour was ready for use. This treatment freed the crude colour from aniline, unaltered rosaniline, and some monophenylated rosaniline, together with the salt. The colouring matter consisted of tri- and di-phenyl rosaniline, together with proportions of monophenylated rosaniline and unaltered rosaniline, all in the form of hydrochlorides, and varying in proportion according to the blueness to which the original melt had been carried, and the care with which the subsequent purification was executed.

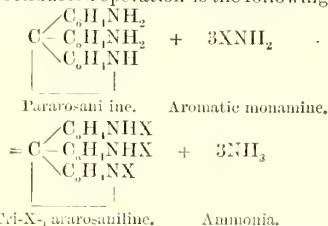
The other process, and the one which has finally survived, consisted first in the preparation of rosaniline base, either by decomposing the arsenate, sulphate, or oxalate with milk of lime, or the hydrochloride with soda. This was heated with aniline and acetic acid, which, however, in time was displaced by benzoic acid, and in the latter form the process is now almost universally carried out.

The function of the acid in the reaction is

exceedingly obscure, and no satisfactory explanation of it has ever been given. In the reaction the acid plays no part, and it can be, as a matter of fact, recovered unchanged from the melt, yet rosaniline base alone cannot be phenylated in this manner, nor, as has already been stated, can its salts with *inorganic* acids.

Again, a very small quantity of acetic acid suffices to cause the phenylation to take place, but there are limits beyond which it is unsafe to reduce it, whilst in the case of benzoic acid the quantity necessary for the reaction is far smaller, but it has a limit correspondingly low, though still well marked.

What takes place, practically quantitatively, in a well-conducted operation is the following:—



In the above, X may represent phenyl, tolyl,  $\beta$ -naphthyl, &c. Friswell in 1878 produced a triphenyltriamido-rosaniline by acting on *p*-rosaniline base with phenylene-diamine.

A good proportion for work is the following:

Rosaniline base	50 parts
Aniline	300 "
Benzoic acid	3 "

The aniline is first introduced into an iron still capable of holding twice the charge usually worked, and provided with an agitator working through a stuffing-box in the top, a swan neck or head communicating with a condenser, and a tube provided with a valve for running out the finished blue melt. A thermometer is inserted in the usual way and a test hole closed with a wooden plug provided, and the still is set in an oil bath, air bath, or, in some cases, even over a naked fire.

The aniline is warmed and the base and benzoic acid then introduced and the heating continued. As soon as a temperature of 100–120° is reached, the base parts with its constitutional water, and at 130–140° the melt enters into brisk effervescence and ammonia comes off in abundance. The heating is steadily pushed on till 180° is reached, when the fire is checked and the further treatment continued with great caution, frequent tests being drawn and examined until the required shade is reached, when the fire is drawn and the melt removed as speedily as possible from the still, slightly cooled, and run into its own volume of methylated spirit. The whole is now quickly raised to boiling when 25 parts by weight of commercial hydrochloric acid is run in and the whole forced through a filter into a crystallising tank of copper where it is allowed to cool slowly for three or four days. It has now become a more or less fluid magma of minute crystals of the triphenylated rosaniline hydrochloride; these are placed on suitably constructed filters and washed with methylated spirit until free from mother liquors.

The mother liquors are rendered alkaline and distilled, whereby the spirit and aniline are recovered for further use, whilst a quantity of basic blue of a red shade and containing the lower phenylated rosanilines &c. is also obtained.

The crystallised substance is known as '*opal blue*' and is insoluble in water but soluble in alcohol, aniline, and mixtures of alcohol and benzene, with great ease. It is used to a moderate extent for dyeing the very finest, or as they are technically known, '*greenest*' shades of blue on cotton on a soap and alumina mordant. The cost of the spirit used to bring the colour into solution, however, entirely prevents its use for general purposes.

For these it is, however, employed in the form of the sodium or ammonium salts of its sulphonic acids, two forms of which, both discovered by E. C. Nicholson, are in common use.

*Nicholson, alkali, or fast blue*, consists mainly of a monosulphonate having the general formula  $XHSO_3$ , where X stands for any given phenylated rosaniline minus an atom of hydrogen. It is prepared by the cautious solution of the hydrochloride of the blue in four times its weight of oil of vitriol with vigorous stirring or mechanical agitation. The mixture may on complete solution be treated in two ways, which consist either in the cautious addition of fuming oil of vitriol of known percentage of  $SO_3$ , or else of gentle heating. Whichever process is applied, the necessary precautions are so obvious as not to need description, and the operation is finished when a test portion drawn from the mass is found, after precipitation in water and freeing by washing on a filter from excess of sulphuric acid, to be soluble in a hot solution of sodium carbonate.

When this point is reached, the whole of the acid melt is precipitated by projection in a thin stream into water which is vigorously agitated. The precipitated sulphonic acid is then thrown on to filters and thoroughly washed until the wash-waters no longer redden blue litmus paper. The pure sulphonic acid is then dissolved in a known quantity of sodium carbonate solution and this evaporated to dryness. The sodium salt is generally ground and appears in the market as a dark-blue powder.

In this form it is mainly used for dyeing woollen goods, and has the peculiar property of dyeing from an alkaline bath, the combination of the colouring matter in the form of the sodium salt with the goods being nearly colourless until the salt is decomposed by immersing the washed goods in dilute acid, or, as it is termed, '*developing*' them.

*Soluble blues*. These are higher sulphonic acids or their salts, and may be generally represented as  $X(HSO_3)_n$ , where  $n$  represents from two to four. The method of preparation is identical with that employed in the manufacture of the Nicholson blues, but the process is pushed further either by the employment of more  $SO_3$  or more heat. The acid treatment is stopped as soon as a portion of the melt is soluble in hot water. The blue acid is then precipitated by the employment of a limited quantity of water, and freed by mechanical means from the main bulk of the acid liquors. The pressed cake is then

dissolved in boiling water, and lime added in the form of milk of lime until the liquid has become distinctly alkaline and lost its intense blue colour. Separation of the calcium sulphate and recovery of the lime salt of the blue mechanically retained by it by means of washing and filter presses follow. The lime liquors or brown liquors are concentrated, freed from the sulphate of lime, precipitated during concentration, and then decomposed by the addition of sodium or ammonium carbonate. Filtration follows as before, and the liquors on evaporation leave the salt of the blue as a more or less golden bronze scale.

This manufacture is carried on on a very large scale, the soluble blues having replaced alkaline blues in the cheaper forms of woollen goods, and being also used for cotton, silk, mixed fabrics of all kinds, leather, &c.

*Diphenylamine blue*. A blue of very fine shade produced by the oxidation of commercial diphenylamine (containing paratolylphenylamine) by means of various agents among which carbon sesquichloride and oxalic acid were the most important. The diphenylamine and oxalic acid were fused together with the addition of acetic acid, and the fused mass maintained at a temperature of  $180^{\circ}$ – $190^{\circ}$  for eight to ten hours; formic and carbonic acids and water escaped, and the melt was judged to be finished when the blue ceased to increase in quantity. By another and very successful mode the diphenylamine and oxalic acid were fused together until the water of crystallisation of the acid had been driven off. The mass was then cast into cakes about 1 inch thick, and these broken into fragments, piled—in such a way that free circulation of air could take place—in trays which were in turn placed in a chamber which could be maintained at about  $110^{\circ}C$ , while a considerable current of air passed through it. Much oxalic acid sublimed unchanged, and was recovered for further use.

The crude blue produced in either way was freed from unaltered diphenylamine by washing with a coal naphtha or with light petroleum. Oxalic acid was removed by water and the blue, after conversion into hydrochloride, was afterwards sulphonated. Used mainly as a soluble blue for very fine shades on silk.

It has been asserted that this blue consisted of triphenylpararosaniline, but there are many reasons for rejecting this view; at any rate it differs greatly from triphenylpararosaniline prepared by the direct phenylation of pararosaniline.

*Methyldiphenylamine blue*. Prepared in a similar manner to the last from methyldiphenylamine.

*Methylene blue*. In 1876 Lanth discovered that paraphenylenediamine heated with sulphur became converted with evolution of  $SH_2$  into a body which contained sulphur, and, on oxidation, produced a violet dyestuff. The same body could be obtained by saturating a solution of paraphenylenediamine with  $SH_2$  and then adding ferric chloride. The colour had no industrial value, but the similar methylated body obtained by treating dimethylparaphenylenediamine with sulphuretted hydrogen and an oxidising agent is manufactured on a considerable scale.



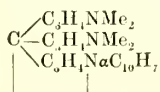
Dimethylaniline is dissolved in hydrochloric acid, and the calculated quantity of sodium nitrite added to convert it into the corresponding nitroso-dimethylaniline; this is very carefully reduced by means of zinc powder, and diethyl paraphenylenediamine is thus obtained; sodium sulphide is added, and an oxidising agent—generally ferric chloride.

A blue and a red body are produced, the former giving a zinc double salt which is easily precipitated by salt brine; the red remaining in solution. A very large number of patents have been taken out for variations in the mode of preparation, some even proposing the reduction of such bodies as the dimethylanilineazobenzene sulphonates and the corresponding  $\beta$ -naphthol colour in order to obtain paraphenylenediamine with separation and recovery of sulphanilic acid or  $\beta$ -naphthol sulphonic acid.

Methylene blue is usually sent into the market as the double zinc chloride. It is found in several shades: the purest are extremely 'green,' but if at all deeply dyed the shades are dull and lifeless. It is also not fast to washing, and does not stand exposure to light very well.

**Victoria blue.** Following on the important discovery of the production of the methyl violets by the action of phosgene  $\text{COCl}_2$  on dimethyl aniline in the presence of anhydrous aluminium chloride came the manufacture of a very fine basic blue colour, introduced into commerce in 1884 under the above name.

To prepare this colour phosgene is mixed with dimethylaniline and aluminium chloride, and gently heated. Tetramethyldiamidobenzophenone is formed immediately, and in almost theoretical proportions. On heating this product with aluminium chloride and phenyl  $\alpha$ -naphthylamine a second condensation ensues, and the



chloride of Victoria blue B, of which the colour base has the formula annexed, is produced. Similar operations with the same ketone and methylphenyl  $\alpha$ -naphthylamine give Victoria blue 4 R, while tetraethyldiamidobenzophenone with phenyl  $\alpha$ -naphthylamine gives Victoria blue 2 B.

Many other similar bodies of a blue or violet colour may and have been obtained by variations of the bodies condensed. R. J. F.

#### ANILINE BROWN AND AZO-COLOURING MATTERS.

**ANILINE SALT.** The commercial name of aniline hydrochloride  $\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$ .

It is prepared in large quantities for the use of calico printers, who employ it in the production of aniline black. The process consists in mixing the calculated quantities of pure aniline and muriatic acid in stone tanks and allowing the salt to crystallise, freeing it from mother liquors in a centrifugal machine and drying. The muriatic acid used should be of good quality, fairly free from iron and absolutely free from even traces of copper, or the salt will rapidly blacken.

The mother liquors may be neutralised with lime or soda, and the aniline recovered, or they may be boiled down and used in making magenta by the nitrobenzol process &c.

'Aniline salt' occurs in commerce in large white nacreous and much contorted plates.

The great desiderata for the calico printer are that the salt should be made from pure aniline and should be dry and normal, containing 93 parts aniline to 36.5 parts of hydrochloric acid; it should be free from sand and grit, which injure the printing machines. R. J. F.

**ANIMAL CHARCOAL.** *Noir d'os*, Fr.; *Knochenschwarz*, Ger. This substance, also known by the name of Bone Black, or technically as 'Char,' is formed by carbonising bones at a high temperature in vessels from which air is excluded. Animal charcoal possesses the property of absorbing organic colouring matters from solutions brought in contact with it; thus a solution of brown sugar passed through animal charcoal will be found to have its colour more or less removed. This property is also possessed, though to a far smaller degree, by wood charcoal, as first noticed by Löwitz about the year 1800. In fact, from that date to 1811, wood charcoal was much employed for decolourising syrups, but it was then demonstrated by Figuier that bone black was far more effectual and energetic in its action. In 1812 Charles Derosne introduced animal charcoal into the manufacture of sugar, and in 1821 Bussy and Payen obtained a prize for a memoir on the properties and mode of action of charcoal. Although the effect of animal charcoal is most conspicuous in removing organic colouring matters from solution, it is also capable of absorbing many other organic and also mineral substances. It was proved by Graham that various mineral substances were removed from solution by animal charcoal; thus, the lime is taken up from lime-water and metallic salts are absorbed from their solutions in water. According to Chevallier, lead nitrate and acetate are completely removed by animal charcoal. Weppen has shown that this action extends to a great variety of metallic salts, including cupric, zinc, chromic and ferrous sulphates, nickel, cobalt, silver, mercurous and mercuric nitrates, tartar emetic, stannous chloride, and ferric acetate.

As the result of a number of experiments on the absorption of different salts by animal charcoal, Bodenbender (*Sugar Cane*, vol. ii, p. 316) has arrived at the following conclusions:—

1. The power which it possesses of absorbing salts is for the most part a physical property.

2. A given weight absorbs a larger proportion of salts from a concentrated than from a diluted solution; on the other hand, the proportion absorbed from a constant quantity of salts is more considerable when this quantity is in a dilute, than when it is in a concentrated solution.

3. The presence of sugar has only a slight influence on the absorption of salts.

4. The salts of potassium are retained in smaller proportion than those of sodium.

5. Among the salts experimented with, the amount taken up is in the following order, beginning with that least absorbed:—potassium chloride, sodium chloride, potassium nitrate, sodium nitrate, potassium acetate, sodium acetate, potassium sulphate, sodium sulphate, magnesium sulphate, potassium carbonate, sodium carbonate, sodium phosphate.

6. A chemical action of the charcoal has been observed with respect to some carbonates,

oxalates, and other salts, being brought about by the presence of calcium sulphate and phosphate in the charcoal.

7. Charcoal saturated with one salt is capable within certain limits of withdrawing another salt from solution.

8. There is less absorption by charcoal of a salt when in contact with it for a short time than when the contact is prolonged. The difference due to time of contact, however, ceases when the contact has lasted some hours.

Various explanations have been offered to account for the peculiar action of charcoal. It is attributed by Bussy to the highly divided state of the carbon contained in it. From the similarity of the action of charcoal upon diverse bodies, and the general nature of its operation, it would appear to be due to some physical or mechanical cause. Charcoal seems indeed to exert merely a surface action, withdrawing the colour from the liquid passed through it, but not in any way destroying the same, and Kohlrausch has shown by experiment, that by means of a solution of ammonia it is possible to practically dissolve out all the colour which has been absorbed by charcoal through which molasses has been previously passed.

It has been suggested that the action is due to absorption of nitrogen and its conversion in the pores of the charcoal into ammonia, but this has been disproved by the fact that the charcoal can be cooled in gases not containing nitrogen, and that under these conditions it still retains an equal decolourising power.

In connection with the action of animal charcoal, it is stated by P. Degener and J. Lack (German Patent, 31,358, 1884) that the freshly ignited charcoal, moistened with as much water as it can take up, and exposed to light and air, produces, even in a few minutes, a perceptible quantity of hydrogen peroxide, and is thus rendered more active than the untreated material.

They also state that exposure for forty-eight hours in layers of 3 inches thick, the charcoal being frequently sprinkled with water and turned over, gives good results, and that if milk of lime is sprinkled over bone black, calcic peroxide is produced, and in the same way other alkaline earths and alkalis can be converted into peroxides.

It was first observed by Tilliot that more organic matter is absorbed by charcoal from solutions at a high temperature than in the cold, this result being only partially due to the increased circulation caused by heating.

*Manufacture of Animal Charcoal.*—The bones employed should be carefully selected, hard, and free from extraneous matter. Horse, whale, and fish bones are not of a suitable character, owing to their yielding a soft char. Bones which have been exposed to atmospheric action for a long time or which have been buried in the ground cannot be successfully employed, as, owing to the alteration in their composition, they yield a char deficient in carbon.

Before proceeding to carbonise the bones, the fat is removed by boiling, or by means of a suitable solvent, such as benzene. By the first-named treatment from 4 to 5 p.c. of fat is extracted, and by the second from 6 to 8 p.c. In

the process of extracting fat from bones by means of a solvent, difficulties arise from the presence of water, and F. Seltsam (Patent 10,208, 1855) has proposed to overcome these by using a solvent (such as a hydrocarbon from petroleum) having a higher boiling-point than that of water, the temperature during extraction being raised to above 100°C. He states that by this means the water is expelled from the bones and the extraction of fat is rendered more complete. Dr. Lorenz says that bones after treatment with benzene contain 1.2 to 2.5 p.c. of fat, which can be extracted by a further treatment with benzene, and 0.48 to 0.8 p.c. of fat removable by ether, or in all, 1.68 to 3.3 p.c., which is lost in the process. This mode of extracting fat is employed in many factories on the continent and in one or two in the United Kingdom, but is objected to by those not using it on the ground that the advantage gained in the increased amount of fat recovered is more than counterbalanced by the lowness of its value owing to its bad quality and disagreeable odour, and also because the char subsequently made is depreciated in value by reason of its containing less carbon.

The apparatus employed in making bone charcoal is similar to that used in a gasworks. The bones are carbonised, after being roughly crushed, in vertical or horizontal iron retorts of a round, oval, or D section, the latter by preference. The length of the horizontal retort is usually from 10 to 12 feet, the long diameter being 18 inches and the short diameter of the oval retort 12 inches. There are usually five retorts in each bed. The retorts are connected, in the same way as gas retorts, with a hydraulic main, and this again with condensers or scrubbers filled with coke in which the bone oil separates and from which the gases are exhausted, and then forced through a series of washers containing water to remove the ammonia, the residual gases, which are employed for heating and lighting purposes, finally passing into a gas-holder. Charges of about 2½ cwt. of bones are carbonised in vertical, and 3½ cwt. in horizontal retorts, the operation taking about six to eight hours with the former and eight to ten hours with the latter. The bone oil collected in the condenser amounts to from 3 to 5 p.c. on the bones carbonised, and the ammonia in the ammoniacal liquor is equal to 9½ to 10 p.c. of ammonium sulphate, into which it is converted in the usual way. When the bones are completely carbonised the charcoal is removed from the retorts and cooled in strong sheet-iron canisters, which are at once covered with closely-fitting lids and luted round the edges, either with charcoal paste or a water lute. The char when quite cold is crushed, generally in a Bogardus mill (on its way to which any iron it may contain is removed by passing over the poles of an electro-magnet) and then sifted into various sizes to suit the requirements of the sugar refiner. It is usually moistened before grinding to keep down the dust. Good bones yield about 65 p.c. of char, but from 20 to 30 p.c. of this is dust, which fetches a lower price than the larger grist.

The following analysis gives approximately the composition of a good sample of bone charcoal:—

Carbon . . . . .	10.51
Calcium and magnesium phosphates, calcium fluoride, &c. .	80.21
Calcium carbonate . . . . .	8.30
Calcium sulphate . . . . .	0.17
Ferric oxide . . . . .	0.12
Silica . . . . .	0.34
Alkaline salts . . . . .	0.35
	100.00

Moisture originally present . . . . . 8.00

Space occupied by one ton of dry bone charcoal, 48 cubic feet.

Sizes left on sieves of various degrees of fineness:—

Above 10 holes to linear inch . . . . .	0
10 to 20 " " " " . . . . .	28
20 to 30 " " " " . . . . .	32
30 to 40 " " " " . . . . .	27
40 to 50 " " " " . . . . .	11
Below 50 " " " or dust . . . . .	2

100

The carbon always contains a certain proportion of nitrogen amounting to about one-tenth of its weight; there is also a minute proportion of hydrogen present. The nitrogen continually becomes less and less, whilst the bone charcoal is being used for sugar-refining.

When char is repeatedly reburned it becomes less porous and shrinks in volume, so that a ton of char, which, when new, measures 48 to 54 cubic feet, may be reduced to as low as 28 cubic feet after being reburned many times, or, in other words, its apparent density may be nearly doubled.

Dr. Wallace has, however, shown that the real sp.gr. varies but little; thus, a new char occupying 50.6 cubic feet per ton, or having an apparent sp.gr. of 0.71, had a real sp.gr. of 2.822, whilst a moderately old sample, occupying 35 cubic feet per ton, or having an apparent sp.gr. of 1.03, had a real sp.gr. of 2.857, or only a trifle over that of the new.

Another proof that char loses its porosity to a considerable extent by long-continued use and reburning is afforded by the fact, pointed out by Dr. Wallace, that dry new char will absorb from 80 to 100 p.c. of its weight of water, whereas old char will only retain from 30 to 45 p.c.

Bone charcoal is sometimes used as a pigment, and is prepared by first making it into a paste with water, and then grinding it to a very fine powder, which is afterwards dried.

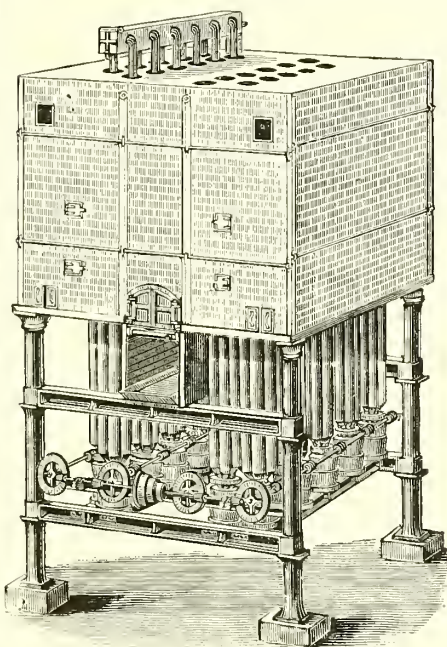
*Ivory black* consists of char in an exceedingly fine state of division.

Bone charcoal is used for the purification of water and also of oil, paraffin, glycerine, &c., and the dust is employed in the manufacture of ivory black and blacking. The chief use of bone charcoal is, however, for decolourising saccharine solutions (*v. SUGAR*).

New charcoal of good quality should, in the dry state, contain not less than 9 nor more than 11.5 p.c. of carbon. The silica should not exceed 0.5 p.c., the oxide of iron 0.15 p.c., and the calcium sulphate 0.2 p.c. New charcoal is usually sold on a basis of 8 p.c. of moisture. The weight of a cubic foot should not exceed 52 lbs.

New charcoal should, when incinerated, leave an ash of a uniform white or cream colour; the presence of grey or reddish particles indicates that the sample has been mixed with old charcoal. New charcoal when brought in contact with the tongue, adheres to it somewhat strongly. The size of grain which it is desirable to have in new charcoal depends upon the use to which it is to be applied. Large grain charcoal is preferable for strong liquors, such as the liquor used for washing loaf sugar. Refiners, as a rule, prefer small grain; if, however, the grain be very small it impedes the passage of liquor and also gives considerable trouble in washing. When bone black has by long use practically lost its power of removing colour, it is known as spent char and is then used as a manure, either as it is, or more generally after treatment with sulphuric acid, so as to form superphosphate of lime.

*Revivification of char.*—A description of the kilns most generally in use for revivifying char will be found in the article on sugar, but of late years these have been to a considerable extent replaced by the Buchanan and Vickess'



kiln. This revolving-pipe and self-discharging kiln consists of 22 cast-iron pipes, each about 1 foot in diameter, placed in a double row on each side of a furnace. Each pipe is fitted with an interior perforated pipe to convey away the steam and other gases evolved. Hollow louvres project over the holes, serving the double object of alternating the position of the char and preventing it from finding its way into the interior pipe, at the same time allowing free egress for the vapour. Attached to each carbonising pipe are six cooling-pipes which are made to revolve slowly with them. A self-discharging apparatus



is placed at the bottom of each set of cooling pipes, and automatically removes measured quantities of char at stated intervals. These kilns are provided with a square main pipe at the top of the carbonising pipes which is heated by the waste gases coming from the interior pipes and serves as a drier for the wet char which is placed over it and, as it dries, runs into the space between the internal and external pipes. This kiln presents advantages over the ordinary kiln, the char being more evenly burned, whilst the pipes, owing to their rotation, are exposed equally to the action of the heat and, therefore, preserve their shape. The use of superheated steam for the purpose of revivifying char has been repeatedly suggested and has been employed on the Continent. The process has the advantage that by means of steam it is possible to regulate the heat applied to any given extent, and it also effects a saving in fuel. Each part of the char gets equally heated and there is no danger of its pores being contracted by over-burning.

Wm. Cornack has patented the use of high pressure and superheated steam and air at not less than 650°F., by which means he claims to be able to revivify char at a black heat instead of a red heat.

Pampe suggests the regeneration of char by means of steam at 600° to 700°C. which renders the char red-hot. He says that the char must be as large as peas, in order that the steam may thoroughly penetrate it.

In the United States the wet char, after it has been used in the refining of sugar, is taken (usually by bands) to the top of driers which are placed on the char kilns between the beds of pipes. The driers are usually of an A section, and extend the whole length of the bed, and they have a hopper at the top into which the char is fed. The char passes through a slit left for that purpose between the sides of the hopper and the top of the drier, and slides down each side on to the beds of the kilns, the char on its passing down being loosely held against the drier by means of an iron louver-arrangement, the laths of the louver being placed a short distance from the drier. The flue-gases, after leaving the kiln, pass through horizontal flues backwards and forwards the whole length of the drier, so that the char is dried by means of the waste heat, and considerable economy is effected in fuel. The cooling-pipes at the lower end of the char pipes are provided with an automatic continuous or intermittent discharging arrangement. This mode of working, besides effecting a saving in labour, causes the char to be better burned, and is advantageous in other respects. In some cases the char after coming from the cooling-pipes is passed through a kind of upright multitubular boiler, the warm char passing through the tubes, which are surrounded with water. This plan of operating avoids the necessity of cooling the char by means of water in the cisterns and economises its heat, which would otherwise be lost.

In addition to the ordinary mode of washing and revivifying char, as mentioned under 'sugar,' various suggestions have been made,

and the most important of these will now be briefly described.

Very dilute hydrochloric acid is often employed for purifying char, especially char which has been used in the manufacture of raw beet sugar. The calcium chloride thus produced is washed out as far as possible by boiling water, and the amount of calcium carbonate is thereby reduced to a notable extent.

In beet sugar factories and in refineries, the char is sometimes allowed to ferment: a little of the 'sweet' being left in it, the acids produced dissolve some of the calcium carbonate and sulphide, forming soluble calcium salts which are afterwards washed out.

Crossfield, Barrow, and Cook took out a patent (2,024, 1874) for the use of a solution of superphosphate in lieu of hydrochloric acid.

Cook had previously patented (2,506, 1872) the use of a solution of ammonium chloride mixed with the char after the latter had been washed. The char after this treatment on being reburned gave off ammonium carbonate, and calcium chloride remained in it, and was afterwards removed by washing.

It has also been suggested to pass the vapour of ammonium chloride through the red-hot char in the kiln pipes, the calcium chloride produced being subsequently washed out. Phillips proposed (Patent 2,049, 1870) the use of alcohol, in conjunction with ammonia, and other alkalis, to remove colouring matters &c. which had been absorbed by char. The alcohol and ammonia were recovered by distillation, and the char so treated was again used without reburning. This process was, we believe, tried on a large scale by Finzel, but was not attended with satisfactory results. Treatment with a solution of boric acid was patented by Lugo and Gandolfo (No. 2,535, 1876).

The use of dry hydrochloric acid gas was patented by Edward Beanes (No. 283, 1864), and this, it was said, only attacked the calcium carbonate, there being no loss of calcium phosphate, whereas when an aqueous solution of the acid is employed, a certain amount of phosphate is always dissolved.

Beanes, Patrick, and many others have proposed to remove the carbonate of lime by means of carbonic acid in the presence of water.

Duncan and Stenhouse have patented the use of dilute nitric acid for purifying char. This process presents the advantage that any calcium nitrate left in the char will be decomposed on heating, and the residual lime can be readily washed out.

The exhaustion of the air out of the char previous to the introduction of dilute hydrochloric or other acid has been frequently suggested, so as to equalise the action of the solvent and prevent, as much as possible, the solution of the calcium phosphate.

Washing by means of an upward current of water was patented by Andrew Stewart (No. 2,488, 1879).

Espeut (Patent 3,589, 1874), De Castro, and others have proposed to fill and empty char cisterns by forcing a mixture of char with liquor or water through a pipe into or out of the cisterns. A difficulty experienced in working this way is caused by the char having a tendency to

block up the pipes. When, however, the distance is short, and a straight and separate pipe can be employed, this mode of working is most satisfactory.

After reburning, the char is usually conveyed to the ear cisterns by means of trucks or bands; but Steel and Hastie in 1868, and since then G. Finzel, proposed to accomplish this removal by means of a current of air. This plan was used by Finzel for the whole of his dry charcoal, but is not at present employed. The objections to using it are that the char is reduced to dust by attrition, and the pores are filled with this dust, the surface of the char at the same time becoming glazed.

After the char has been removed from the kilns, it is sometimes sifted to remove dust. The dust may also be advantageously got rid of by the use of Mumford and Moodie's separator, in which a circulating current of air is employed for this purpose. N. Bros.

**ANIMAL OIL** *v.* BONE OIL.

**ANIME** and **ANIMI** *v.* OLEO-RESINS.

**ANIMIKITE.** A mineral from Silver Islet Mine, Lake Superior.

As	Sb	S	Hg	Ag	Co	Ni	Fe	Zn
0.35	11.18	1.49	0.99	77.58	2.10	1.90	1.68	0.36

Loss 1.68 = 99.31 sp.gr. 9.45 (Wurtz, J. 33, 11403).

**ANISEED** (*Anis*, Fr. Ger.). The fruit of the *Pimpinella Anisum*, cultivated in Malta, Spain, and Germany. Used for the preparation of anise oil and cordials. Alcohol extracts 36.24 p.c. of this spice (Biechele, Ph. [3] 10, 878).

**ANISE CAMPHOR** *v.* CAMPHORS.

**ANISE OIL.** The essential oil of aniseed obtained by distilling it with water. According to Landolph (C. R. 81, 97; 82, 226), it contains 90 p.c. of *anethol*, boiling at 226°C. Anethol, according to Perkin (C. J. 32, 668), is *p*-allyl-anisol  $C_6H_4(OMe)CH:CH.CH_3$ ; he obtained it by heating *p*-methoxy-phenylcrotonic acid.

Anise oil is sometimes adulterated with fennel oil; this can be detected by heating the oil, when the fennel odour becomes perceptible.

Star anise oil has a similar colour and taste, but it does not solidify at 2°C.

**ANISIDINE**  $NH_2.C_6H_4.OMe$ . *Orthanisidine*. Obtained by the reduction of orthonitranisol with tin and hydrochloric acid or iron and hydrochloric acid (Meister, Lucius, and Bräning, Germ. pat. 7,217 of Dec. 3, 1878), is a colourless oil which boils at 226.5° at 734 mm. pressure (Müllhäuser, A. 207, 239), at 216°, and has a sp.gr. = 1.108 at 26° (Brunck, Z. 1867, 205). When diazotised and treated with  $\beta$ -naphtholdisulphonic acid (R-acid), it yields anisol-red (*v.* AZO-COLOURING MATTERS). A mixture of orthanisidine (2 mols.) and paraphenylenediamine (1 mol.) is converted, on oxidation with potassium bichromate, into a reddish colouring matter formerly employed under the name safranisol (Kalle & Co., Germ. pat. 24,229 of Oct. 27, 1882; expired March 1885).

**Paranisidine**, obtained from paranitranisol by reduction with tin and hydrochloric acid, crystallises in prisms which melt at 52° (Brunck, *l.c.*), at 55.5°–56.5° (Lossen, A. 175, 324), and boil at 245°–246° (Salkowski, B. 7, 1009).

**ANISIDINE PONCEAU** *v.* AZO-COLOURING MATTERS.

**ANISOCHILUS CARNOSUS.** An Indian plant belonging to the Labiatae containing a volatile oil. Used in quinsy (Cooley, 1).

**ANISOL** *Anisöl*; *methylphenyl ether*  
 $C_6H_5.O.CH_3$ .

**Preparation.**—Anisol can be obtained by distilling anisic acid or *o*-methoxybenzoic acid with baryta, or by heating potassium phenate with methyl iodide at 120° (Cahours, A. Ch. [3] 2, 274; 10, 353; 27, 439). It is prepared by passing a current of methyl chloride over dry sodium phenate heated at 190–200° (Vincent, *Bl.*, 40, 106).

**Properties.**—It is a colourless ethereal liquid, which boils at 155–155.5° at 762.3 mm. (Schiff, A., 220, 105) and has a sp.gr. = 0.991 at 15°.

**ANISOL RED** *v.* AZO-COLOURING MATTERS.

**ANISOMFELES MALABARICA.** A much esteemed Indian plant belonging to the Labiatae; an infusion of the leaves is used in intermittent fevers, and the essential oil is applied externally in rheumatism (Cooley, 1).

**ANKCOL, AKOLA, DHERA BARK.** The root bark of *Alaungium Lamaeckii*, one of the Cornaceae, used in leprosy and skin diseases (Dymock, Ph. [3] 9, 1017).

**ANNAITO, ARNAITO, ARNOITO, or AN-NOITO.** (*Rocou* or *roucou*, Fr.; *Orlean*, Ger.) A colouring matter derived from the fruit capsules of the *Bixa Orellana*, an evergreen plant growing in the East and West Indies, and more especially in South America, where it is principally prepared. Two kinds are imported: Spanish annatto made in Brazil, and the flag or French, prepared mostly in Cayenne, which has rather a putrid smell.

The fruit capsules contain a large number of seeds embedded in a pulpy reddish-coloured fruit flesh, similar to that surrounding the seeds of the ripe tomato. Three methods are adopted to obtain the colouring matters. The first is to rub or wash off the colouring matter with water, allow it to subside, and expose it to spontaneous evaporation till it acquires a pasty consistence; the second is to bruise the seeds, mix them with water and allow them to ferment until all the colouring matter is removed from them; the third is to boil the seeds with water till a thick paste is obtained, but the resulting product is not so good as in the former processes.

The decoction of annatto in water has a strong peculiar odour and a disagreeable taste. Its colour is yellowish-red, and it is slightly turbid. In alkaline solution its orange-yellow is clearer and more agreeable to the eye. If annatto is boiled in water with an alkali, it dissolves much better than if alone, and the liquid has an orange hue. Acids precipitate the annatto as an orange-coloured precipitate.

To prepare an annatto dye-bath the annatto is cut up into small pieces and boiled for some seconds in a copper with its own weight of pearl ash, provided the shade required does not want less alkali. The fabric may be dyed in this bath, either by these ingredients alone, or by adding others to modify the colour.

The colour, however, is so fugitive that its employment is restricted.

An annatto solution is also used to dye cheese and butter.

Lawson (P. J. [3] 16, 645) gives ten analyses of various annattos, the amount of colouring matter varying from 1 to 12 p.c. A sample of a good annatto analysed by Wynter Blyth contained colouring resin 28·8, ash 22·5, extractive matter 24·5, water 24·2.

Annatto contains a yellow crystalline colouring matter *bixin*  $C_{16}H_{22}O_2$  which on treatment with alkalis, in contact with the air, absorbs oxygen and passes into *bixein*.

**ANNEALING or NEALING** (*le recuit*, Fr.; *das Anlassen*, Ger.). A process by which glass is rendered less fragile; and metals which have become brittle, either in consequence of fusion or long-continued hammering, are again rendered malleable. When a glass vessel is allowed to cool immediately after being made, it will, if a small splinter of flint or an angular fragment of quartz is dropped gently into it, fly to pieces with great violence, sometimes immediately, sometimes after a few minutes. This extreme fragility is prevented by annealing, or placing the vessels in a hot oven, where they are allowed to cool slowly, the process lasting several hours, or even days.

Similar phenomena are exhibited in a higher degree by glass-tears, or Prince Rupert's drops, produced by letting drops of melted glass fall into cold water. Their form resembles that of a pear, rounded at one extremity and tapering to a very slender tail at the other. If a part of the tail be broken off the whole drop flies to pieces with a slight explosion; and yet the tail of a drop may be cut away by a glass-cutter's wheel, or the thick end may be struck smartly with a hammer, without inducing disintegration. When heated to redness, and permitted to cool gradually, they lose these peculiarities, and do not differ sensibly from common glass. The peculiar brittleness of unannealed glass is, by many manufacturers, referred to the following conditions. The exterior surface of the glass cooling more quickly than the layers of glass beneath, the two portions of glass are supposed to be in different states of tension; as it is technically expressed, *a stretched skin of glass* is formed; and as this film differs in the arrangement of its particles from those parts which have cooled more slowly, there is a constant tendency to fracture, the slightest scratch upon this skin disturbing the entire molecular arrangement. If any mass of glass or of metal cools rapidly, there will be, according to the thickness of the mass, a greater or less difference between the arrangement of the constituent particles on the outer and inner portions. The process of annealing secures an equal arrangement throughout the mass.

When metals have been extended to a certain degree under the hammer, they become brittle and incapable of being further extended without cracking. In this case the workman restores their malleability, sometimes by annealing, or, in other cases, by heating them to redness and allowing them to cool slowly. The rationale of this process seems to be, that the hammering and extension of the metal destroys the kind of arrangement which the particles of the metal had previous to the hammering, and that the annealing, by softening the metal, enables it to recover its original structure. U.

**ANNOTTO** v. ANNATTO.

**ANONA MURICATA.** A decoction of the root is used as an antidote for fish-poisoning, and the bark serves as an astringent. The leaves are useful in softening abscesses, and from the seeds a wine can be prepared which is said to be beneficial in cases of diarrhœa (C. Z., 10, 433; S. C. I., 5, 332).

**ANTHEMOL** v. CAMPHORS.

**ANTHOKIRIN.** The yellow crystalline matter of the flowers of the yellow toadflax (*Linaria vulgaris*). Formerly used as a dyeing material, but the colour is not permanent.

**ANTHOKYAN.** The expressed juice of the sweet or purple violet (*Viola odorata*), gently heated to 89°C., then skimmed, cooled, and filtered. A little rectified spirit is then added, and the following day the whole is again filtered. Used to make syrup of violets, and to colour and flavour liqueurs (Cooley, 1).

**ANTHRACENE**  $C_{14}H_{10}$ . Discovered by Dumas and Laurent in the highest boiling portion of coal-tar, and termed by them *paranaphthalene* (A. 5, 10); further examined by Laurent, who re-named it anthracene (A. 34, 287); first obtained pure and its composition determined by Fritzsche (A. 109, 249), and more exactly studied by Anderson (A. 122, 294; C. J. 15, 44).

*Occurrence.*—Anthracene is one of the products of the destructive distillation of coal, and is found in the tar; the average yield of the pure hydrocarbon is about 0·3 per cent. of the tar obtained.

A new source of anthracene has been announced (D. P. J. 246, 429) in the tar obtained when the residue, left after the illuminating oils have been distilled from Baku petroleum, is allowed to fall on pumice in red-hot iron retorts. 1,000 kilos of naphtha residue under these conditions yield 500 c.m. of gas, used to heat the retorts, and 300 kilos of tar, containing about 0·2 per cent. of pure anthracene. The supply of the naphtha-residue is, however, too limited to render anthracene from this source a serious competitor with that from coal tar.

According to Elliott (Am. 6, 248), the tar obtained in the manufacture of gas by the destructive distillation of light petroleum naphtha boiling below 150° contains 2·63–2·90 p.c. of anthracene. A remarkable production of anthracene during the distillation of the higher boiling portions of crude phenol has been observed by Köhler (B. 18, 859).

*Preparation* (Auerbach, Das Anthracen und seine Derivate; Kopp, J. 1878, 1187; Perkin, Journ. Soc. Arts, 27, 572).—Anthracene is obtained from the 'green grease' which forms the last portion of the 'heavy oil' or 'dead oil' of the tar distiller; this at first is a brown liquid with a green fluorescence, but soon becomes semi-solid on standing owing to the separation of solid substances. When no further separation occurs, the mass is subjected to filtration, either in a centrifugal machine or a filter press, first in the cold and finally at 40° (Gessert, D. P. J. 196, 543), or is filtered through strong linen bags, and afterwards submitted to hydraulic pressure in a press so arranged that the plates can be heated with steam and the cake hot-pressed. A notable quantity of anthracene remains dissolved in the expressed oil, and especially in



the portions separated when the temperature is raised, and is recovered by redistilling and working up the product as just described. The hard yellowish-green cake obtained, containing 25-40 per cent. of pure anthracene, is ground to a fine powder in mills and heated with coal tar naphtha (b.p.  $80^{\circ}$ - $100^{\circ}$ ), or petroleum spirit (b.p.  $70^{\circ}$ - $100^{\circ}$ ), in large iron vessels provided with stirrers. Petroleum spirit is to be preferred (Perkin) since it dissolves less anthracene, whilst the impurities are sufficiently soluble in it to be removed if the quantity of solvent employed is 2-3 times as great as that of the anthracene to be purified. The residue contains from 45-50 per cent. of the hydrocarbon, but inasmuch as it is not readily reduced to powder, and unless finely divided is only slowly attacked by oxidising agents, it is sublimed by passing steam, heated at  $220^{\circ}$ - $240^{\circ}$ , over the melted product, and condensing the vapours in a chamber by jets of water. The anthracene thus obtained is in leafy masses, containing from 50-60 per cent. of the hydrocarbon, the chief impurities consisting of carbazole (10-12 p.c.), phenanthrene, pyrene, chrysene, and other hydrocarbons, together with small quantities of phenols of high boiling-point and of acridine; it can readily be ground to a paste, and is now sufficiently pure for conversion into anthraquinone by oxidation. If, however, dichloranthracene is required, further purification is necessary; this can be effected by distillation with caustic potash, whereby impurities such as carbazole and bodies of a phenolic character are retained, and anthracene, together with phenanthrene, distils over with no greater loss than occurs if the 60 p.c. product is distilled alone; caustic soda cannot be substituted for the potash, since it produces no purification of any consequence. Instead of distilling washed anthracene (100 parts) with caustic potash, Perkin employs a mixture of Montreal potash (30 parts), which usually contains potassium hydroxide in considerable quantities, and caustic lime (6 parts). Unless lime is used the residue in the retorts forms a hard cake, which can be removed only with difficulty. Hydrogen is evolved during the distillation. The distillate is freed from phenanthrene by washing with coal-tar naphtha, and the residue is a very pure anthracene. This production of phenanthrene, even from anthracene which has been freed from this impurity by extraction with solvents previous to distillation with caustic potash, is noteworthy and points to the probable existence of molecular compounds of phenanthrene with other of the impurities of the washed anthracene, which are destroyed during the distillation with caustic potash. This process of Perkin has been subjected to considerable criticism. According to Auerbach, a loss of anthracene to the extent of 10 p.c. occurs, and this, added to the cost of fuel employed, renders it the most costly method of purification yet devised. The great advantage of the method, however, is that it brings anthracenes of different origins to a similar condition of purity; even pitch anthracene—obtained by the distillation of gas-tar pitch in iron retorts with the aid of superheated steam, and generally unsuitable for purification owing to the difficulty of removing higher hydrocarbons associated with it—works per-

fectly well after it has been subjected to this process.

An important modification in the method of purifying crude anthracene, based on the far greater solubility of the impurities in mixtures of aniline, pyridine, or quinoline bases, has been patented by the Chemische Fabriks-Aetiengesellschaft in Hamburg (G. P. 42,053 of April 15, 1887). The crude anthracene is dissolved at  $100^{\circ}$  in 1½-2 times its weight of a dehydrated and rectified mixture of tar bases (pyridines) separated from the light oil obtained in tar distillation (compare G. P. 34,947 and 36,372), and the solution, on cooling, yields a crystalline separation of anthracene almost free from carbazole and its homologues. The patentees state that a 33 p.c. anthracene dissolved in 1.75 times its weight of pyridine bases yields on crystallisation an 82.5 p.c. anthracene, whilst when dissolved in twice its weight of a mixture of equal parts of pyridine bases and benzene, it yields an 80 p.c. anthracene, and in twice its weight of a mixture of equal parts of benzene and aniline a 75 p.c. anthracene. The recovery of the anthracene contained in the mother liquors offers no special difficulty.

Remy and Erhart (G. P. 33,417 of Jan. 19, 1886) have proposed crystallisation from oleic acid as a means of purification of crude anthracene. The difficulty of recovering the anthracene contained in the mother liquors would seem, however, to deprive this method of technical importance.

Graham (C. N. 33, 99, 168) has devised a method for recovering anthracene from the filtered oils used in its purification.

A troublesome impurity in anthracene is a peculiar paraffin, which has a high melting-point, and is only sparingly soluble either in light petroleum or coal-tar naphtha; it is dissolved to a certain extent by these solvents when hot, but on cooling is almost entirely deposited again. A small quantity left in the anthracene frequently impedes succeeding operations, and, owing to its stability, passes through most of the processes without change.

*Syntheses*, from orthotolylketone, by heating with zinc-dust (Behr and Van Dorp, B. 7, 17); from orthobenzylbromide by the action of sodium (Jackson and White, B. 12, 1965); and from a mixture of benzene, acetylene tetrabromide, and aluminium chloride (Anschütz, A. 235, 156).

*Properties*.—Anthracene crystallises in glistening white scales, which melt at  $213^{\circ}$ , and boil at a few degrees above  $360^{\circ}$  (Crafts, J. 1878, 67). When pure it shows a bluish-violet fluorescence, but this is concealed if small quantities of yellow impurities (Fritzsche's chrysogen) are present. Yellow-coloured anthracene, on exposure to sunlight, is bleached, and becomes fluorescent, but under these conditions the hydrocarbon undergoes conversion into paranthracene—a peculiar modification, which is much less soluble than anthracene, is unattacked by bromine and nitric acid at  $100^{\circ}$ , and does not combine with picric acid; it melts at  $241^{\circ}$ , and is thereby converted into ordinary anthracene (Fritzsche, J. pr. 101, 333; Graebe and Liebermann, A. Suppl. 7, 264; Schmidt, J. pr. [2] 9, 248). The fluorescence of anthracene and cer-

tain of its derivatives has been referred by Liebermann to a particular molecular grouping (B. 13, 913). The solubility of anthracene in 100 parts of various solvents has been determined by Versmann (J. 1874, 423), Perkin (Journ. Soc. Arts, 27, 598), and v. Becchi (B. 12, 1978), with the following results:—

	Parts of anthracene
Alcohol (absolute) at 16° dissolves	0.076 (B.).
b.p. "	0.830 (B.).
" "	0.591 (V.).
" "	0.574 (V.).
" "	0.491 (V.).
" "	0.475 (V.).
" "	0.460 (V.).
" "	0.423 (V.).
" "	1.175 (V.).
Ether . . . . .	1.736 (V.).
Chloroform . . . . .	1.478 (V.).
Carbon bisulphide . . . . .	0.444 (V.).
Acetic acid . . . . .	0.394 (V.).
Light petroleum . . . . .	
b.p. 70° 10.3°	
at 15° dissolves	0.115 (P.).
Benzene . . . . .	1.661 (V.).
b.p. 80°-100°	0.976 (P.).
Toluene . . . . .	0.920 (B.).
at b.p. "	12.940 (B.).

When introduced into an alcoholic solution of picric acid saturated at 30°-40°, anthracene forms a picrate  $C_{14}H_{10}, C_6H_3(NO_2)_3O$ , crystallising in glistening red needles which melt at 138°; it is decomposed into its constituents by alcohol, water, and dilute alkalis, even in the cold. On oxidation with potassium dichromate or manganese dioxide and sulphuric acid, anthracene is converted into anthraquinone, whilst strong nitric acid oxidises it to anthraquinone and dinitroanthraquinone; nitro-derivatives of anthracene can, however, be prepared by the action of strong nitric acid on the hydrocarbon if care is taken to decompose any nitrous acid which may be formed during the reaction (Perkin, C. S. Proc. 1889, 13). Concentrated sulphuric acid converts anthracene into two isomeric disulphonic acids, and these on oxidation yield two anthraquinonedisulphonic acids, which are isomeric with the two acids obtained by the direct sulphonation of anthraquinone. Anthracene is readily attacked by chlorine and bromine, and yields with each element a series of additive and substitution derivatives; additive compounds, apparently, are the first products of the action, and these either decompose during the reaction or can be decomposed by boiling with alcoholic potash into the corresponding substitution derivatives, which also form additive compounds by the further action of the halogens. Reducing agents, such as sodium amalgam or phosphorus and hydrogen iodide, convert anthracene into the dihydride (Graebe and Liebermann, *l.c.*; Liebermann and Töpf, A. 212, 5).

*Estimation*.—Luck (B. 6, 1347); Meister, Lucius, and Brüning, D. P. J. 224, 559; Nicol (C. J. 1876, 2, 553). The percentage of anthracene in a sample of the commercial product is determined by oxidising it to anthraquinone with chromic acid, dissolving the product in sulphuric acid, and precipitating with water, since the associated impurities are either destroyed during the oxidation or are converted into sulphonic acids soluble in water. The

details of the process are as follows: 1 gram of anthracene is introduced with 45 c.c. of acetic acid into a flask connected with a reversed condenser, and heated to boiling; a solution of 15 grams of chromic acid in 10 c.c. of acetic acid and 10 c.c. of water is then added, drop by drop, to the boiling solution during a period of two hours; and the product is boiled for two hours longer, allowed to stand for twelve hours, then poured into 400 c.c. of water, and, after standing for three hours longer, is filtered. The anthraquinone on the filter is washed with water, with hot dilute alkali, and then with hot water; afterwards it is placed in a small dish, dried at 100°, and digested for ten minutes with 10 times its weight of fuming sulphuric acid at 100°. The solution of anthraquinone in sulphuric acid is then allowed to remain for twelve hours in a moist atmosphere, mixed with 200 c.c. of water, and the precipitated anthraquinone filtered off and washed first with water, then with dilute alkali, and finally with water; it is then dried at 100° in a dish, weighed, ignited, and the ash deducted from the first weighing. The difference gives the weight of anthraquinone corresponding to the amount of anthracene present in the sample.

**ANTHRACENE GREEN.** *Cærulein v. ALIZARIN AND ALLIED COLOURING MATTERS.*

**ANTHRACENE RED v. ALIZARIN AND ALLIED COLOURING MATTERS.**

**ANTHRACENE VIOLET.** *Gallein v. ALIZARIN AND ALLIED COLOURING MATTERS.*

**ANTHRACITE v. FUEL.**

**ANTHRACOXENE v. RESINS.**

**ANTHRAFLAVIC ACID v. ALIZARIN AND ALLIED COLOURING MATTERS.**

**ANTHRAGALLOL v. ALIZARIN AND ALLIED COLOURING MATTERS.**

**ANTHRAPURPURIN v. ALIZARIN AND ALLIED COLOURING MATTERS.**

**ANTHRAQUINONE v. ALIZARIN AND ALLIED COLOURING MATTERS.**

**ANTHRAQUINONE RED v. ALIZARIN AND ALLIED COLOURING MATTERS.**

**ANTHRARUFIN.** 1:4 *Dioxyanthraquinone v. ALIZARIN AND ALLIED COLOURING MATTERS.*

**ANTHROL**  $C_{14}H_{10}O$  or  $C_6H_4(C_2H_5)_2C_2H_4OH$  is obtained by fusing anthracene-sulphonic acid with caustic soda. White crystalline substance, insoluble in ammonia, soluble in caustic potash, giving a yellow solution with green fluorescence. Its alcoholic solution shows a violet fluorescence. With oil of vitriol it gives a yellow solution which becomes blue on heating (Liebermann a. Hörmann, B. 12, 589; L. a. Hagen, B. 15, 1427; L. a. Bollert, B. 15, 226; A. 212, 26, 49).

**ANTIAR RESIN** or **UPAS ANTIAR.** A green resin which exudes from the upas tree (*Antiaris toxicaria*, order Urticaceae). Light petroleum and benzene extract from it a substance analogous to caoutchouc, a fatty matter, and two resinous substances; alcohol extracts from the residue a very poisonous glucoside, *antiarin* (De Vry a. Ludwig, J. pr. 103, 253).

**ANTIARIN v. GLUCOSIDES.**

**ANTI-CHLOR.** Linen and cotton fibre and paper pulp are apt to retain some free chlorine from the hypochlorite used in bleaching,

and as this causes the material to rot slowly, the manufacturers use certain reagents known as 'anti-chlors' to remove the last traces of chlorine. The first substances employed were the neutral and acid sulphites of soda (sodium sulphite and bisulphite); these were superseded in 1853 by sodium hyposulphite, which is now very largely employed. Calcium sulphide, made by boiling milk of lime with sulphur; stannous chloride in hydrochloric acid with subsequent treatment with sodium carbonate to neutralise any free acid; ammonia, and sodium nitrite have also been recommended.

**ANTICORROSIVE COMPOSITIONS AND METHODS.** The surfaces of the various metals such as iron, zinc, brass, &c., which have to be protected from corrosion, are treated in very different ways, thus brass is generally coated with lacquer and zinc with tar, black varnish, or common paint; on the other hand, iron and steel surfaces require a special treatment and it is to this that attention will be given in this article.

There are three conditions to which these surfaces are exposed. First, simple exposure to the atmosphere; second, exposure to cold, fresh, or salt water; and third, exposure to hot salt water.

Iron used under the first conditions can be protected by three methods, each of which has its advantages. First, painting or varnishing. Second, 'galvanising,' that is, coating with zinc by immersing the iron after cleaning by treatment with acid and scouring in a bath of molten zinc; and lastly, by the Bower-Barff process, which consists in exposing the iron at a dull red heat to the action of steam, when a thin adherent coating of magnetic oxide of iron is formed over the metal. This coating seems to withstand atmospheric influences very well indeed.

When required to withstand the action of cold water, the iron may be prepared by the process invented by the late Dr. R. Augus Smith, and which is in almost universal use for water-pipes, viz., coating the surface of the iron with hot tar; but when we come to the protection of iron from the action of cold salt water, the coating must be very frequently renewed or special methods must be employed.

In the case of piers below water frequent recoating is impossible, and recourse must be had to galvanic methods to preserve the metal from corrosion. The simplest and most efficacious way is to bring into contact with the iron a piece of a more easily oxidisable metal like zinc, so that the same liquid may act upon both and generate a gentle galvanic current. As long as the electro-positive metal lasts, the iron is perfectly preserved.

A series of experiments conducted with the object of testing the preservation of iron by this method seemed to show that when the zinc becomes coated (as is the case in sea-water), with oxychloride, its power of preservative action ceases, but further experiments have demonstrated that this negative result was owing to the zinc having only been in mechanical touch with the iron, and not connected with it by soldering. It appears that when zinc and iron are bolted together the zinc becomes most actively attacked near the point of contact, and as the molecular volume of the oxychloride formed

is greater than that of the zinc, the salt formed acts as a wedge and forces the iron and zinc asunder, thus breaking their electrical contact, so that the protective action of the zinc soon ceases. Soldering obviates this, and thorough protective action is maintained till all the zinc is consumed.

In the case of hot sea-water, the method above sketched is the only real anticorrosive process known to be successful. One further precaution, however, requires to be taken. The zinc requires to be rendered thoroughly malleable, because cast zinc rapidly crumbles away in boiling sea-water. It seems that the oxychloride formed penetrates between the faces of the crystals in the mass of the cast zinc and acting like wedges splits the whole mass into fragments.

In an apparatus called the 'Electrogen,' for applying these principles to marine boilers, the zinc is cast as a sphere on a copper conductor, thus giving a considerable mass of metal so as to last some months without renewal. The zinc is then rendered malleable, and the conductor is soldered to the boiler. The whole internal shell of the boiler thus becomes the negative plate of a battery, so that as long as the zinc lasts no corrosion takes place. In cases where the boiler has a steel shell and malleable iron tubes, the latter are often corroded through in a few weeks, as they act as a positive metal to the steel, but when the 'electrogen' is attached to them the same tubes show no deterioration after five years.

Batteries outside the boiler have been tried in which the negative pole is soldered to the outside of the boiler and the positive pole passed insulated through a stuffing-box into the water in the interior, but boiling salt water is too good a conductor, and the current takes the shortest circuit from the positive pole to the boiler, and all more distant parts of the boiler corrode, as though no battery were used. Only by making the boiler one element in a galvanic couple can complete protection be secured. J. L. H.

**ANTI-FEBRIN.** A trade name for acetanilide or phenylacetamide  $C_6H_5NHCO.CH_3$ . Discovered by Gerhardt in 1853, and investigated as an antipyretic by Kussmanl in 1886 (*v. ACETANILIDE*).

**ANTI-FOULING COMPOSITIONS.** The attachment of marine organisms to the bottoms of ships has always been a source of trouble and expense to shipowners. When the growths become luxuriant, not only is the speed of the vessel very much diminished, but, in a sailing-ship, much more lee-way is made. In ordinary trading steamships having a speed of eleven knots per hour it is quite common to have the speed reduced to seven-and-a-half to eight knots by the adhesion of seaweed and shell-fish. Considering that fuel is being consumed at the usual rate, and that wages, interest on capital, depreciation, and general expenses are running on, it will be seen what a serious loss a foul ship entails.

In the case of wooden ships, not only do they foul, but the wood is rapidly destroyed by boring worms, so that it becomes necessary to protect the wood by sheathing the ship with copper. This prevents in great part the adhesion of either plants or shell-fish, but more especially



the former. The writer has in his possession oysters which grew on the copper of a ship at anchor, and which had attained the diameter of over two inches and seemed quite healthy, although the shell adhering to the copper, as well as the part of the mollusc touching that shell, were very dark green. The dark green colour was not caused by copper, as not a trace could be found on analysis, but seemed to be due to some physiological change in the substance of the shell-fish itself.

That the anti-fouling effect is due, however, to the solution of the copper is amply proved by the experiments of Davy and others. Davy tried to economise the consumption of the copper on the ship's bottoms by attaching a more positive metal, such as zinc or iron, to the metal sheathing, so that, by forming a galvanic couple, no copper would dissolve so long as the zinc or iron lasted, the copper being maintained in an electro-negative state. This was followed by the fouling of the ship, and Davy modified his plan by attaching only a few small pieces of iron to the copper, so that a certain amount of solution would take place, sufficient to prevent fouling, yet not sufficient to cause the rapid solution of the copper which was the usual case. The plan was not very successful, as it was most difficult to balance the destructive and preservative actions—a difficulty which constitutes the great obstacle towards obtaining uniformly good results in the anti-fouling compositions on iron ships at the present time. The introduction of Muntz's metal gave a material which, while more insoluble than copper, yet dissolved sufficiently to prevent fouling, and which was at the same time cheaper.

With the introduction of iron into ship-building came an entirely new problem. Copper was quite inadmissible, as it would cause the rapid destruction of the iron wherever it became accidentally exposed to the water.

The class of anti-fouling compositions at first introduced for iron ships, and which are still much used, were what may be called 'mechanical' anti-fouling compounds. First amongst them comes a mixture of white oxide of zinc and tallow, which acts chiefly by failing to give the barnacles or seaweed proper foothold. When a ship which has been coated with such a composition is periodically examined, it will be seen that, after being in the water a short time, minute barnacles and very short sea-grass may grow upon it; but whenever these become of a size to offer an appreciable resistance to motion through the water, they slide off the soft grease to which they have attached themselves. The ship is generally first coated with some common oil paint, such as a mixture of white and red lead in oil, and the mixture of 'zinc and tallow' laid on hot over it. The latter is generally prepared by stirring white oxide of zinc which has been ground in oil into melted tallow, and colouring with some red pigment, generally oxide of iron, till a warm pink colour is attained. The 'zinc and tallow' paint is still in much favour for coating iron sailing-ships.

Many other 'mechanical' anti-fouling compositions have been invented and applied with more or less success. For instance, 'rosin grease' (a compound made by treating the dis-

tillate of common rosin with milk of lime) is thinned with coal-tar oil, and additional rosin added, and, in some cases, creosote and colouring matters, including Scheele's green. Such mixtures form a thick, dark-green grease, which is applied hot, and is sometimes very efficacious. All compositions based on rosin grease have this great drawback, however, that after being in the water several months they become transformed from a grease to a light-coloured porous powder, which allows of free ingress of the sea-water, and, if the preparatory painting has not been very good, very rapid corrosion takes place.

And here may be mentioned one of the most difficult points in connection with the coating of ships. The iron is invariably rough, often pitted and honeycombed deeply, and the surface covered with a fine slime of young sea-grass. In our damp climate, especially in the six months of winter, the bottom after being scraped remains wet, and any paint applied goes on to a wet, and often, a very dirty surface. Hence oil paints are not very successful, except when used in summer, or exceptionally warm dry weather, and even spirit paints may have to be applied in circumstances so very adverse that they come off and leave the ship bare in a few months.

With modern steam vessels the use of any of these mechanical anti-fouling agencies is entirely out of the question, as the velocity of the ship through the water causes it to rub all the greasy paint off. It became, therefore, necessary to devise some chemical anti-fouling substance which would by its poisonous nature prevent the adhesion of marine life to the ship. Copper, of course, at once suggested itself, and compounds of copper were freely tried, but seemed to give the most divergent results. The reason is not far to seek. The copper had to be kept entirely clear of the iron, because of the great danger of corrosion by electrical action, and yet to be of any use the copper must be allowed to dissolve. When the copper, either as a compound, or as spongy copper deposited on zinc, which is used in some patents, is made up in a good varnish like copal and applied to a ship, the result is that the barnacles grow quite as luxuriantly as on wood, because the copper is safely sealed up and cannot be dissolved by the sea-water. The same result may be seen by varnishing a portion of the copper on the bottom of a ship, when vegetation and shellfish take root at once. The problem, therefore, is to get the chemical anti-fouling substance made up in such a medium as will not seal it up, but allow of its gradual solution in the sea-water so as to poison the marine growths. With copper this is dangerous, as on solution it is electrically deposited on any accessible parts of the iron in the neighbourhood, thus causing rapid corrosion.

There is no doubt that could a composition be prepared which would contain sufficient carbolic acid to be slowly given out during a year, and which would prevent its immediate solution, a very perfect anti-fouling coating would be obtained, as all experiments have demonstrated its efficacy. But as yet all phenol mixtures yield up their soluble constituents to the sea-water in a few weeks, and the vessel fouls rapidly after the supply of carbolic acid has become exhausted.

Many poisons, which, like arsenic, are very efficacious against terrestrial life, are not at all successful as anti-fouling agents. We have, as an instance, the failure of arsenite of copper to maintain a clean ship. But the most effective antiseptic known, viz. mercuric chloride, is found also to be the most active anti-fouling agent as yet discovered. Being a readily soluble salt it cannot be directly applied in a paint. Some insoluble compound of mercury must be introduced into the paint which will yield mercury chloride by contact with sea-water. The substance which lends itself most readily to this reaction is mercuric oxide, and this compound is preferred in most good anti-fouling compositions.

The difficulty in obtaining uniform success, even with this agent, lies entirely in the nature of the medium in which it is applied. As the oxide is a basic body it combines with many of the gums used in making varnishes, and forms a substance too slightly soluble in sea-water to be of much use in preventing marine growth. Then, again, good varnishes must be avoided, as they hermetically seal up the oxide, and so prevent solution.

A simple shellac varnish in methylated spirit, with a certain proportion of common rosin and crude turpentine, or Stockholm tar, added so as to render the varnish so soft that its surface is slightly eroded by the action of the sea-water, forms a very suitable medium for the application of the mercuric oxide to the bottom of a ship. Or, if spirit of turpentine be preferred as a solvent, then a varnish of gum dammar and pale resin forms a very suitable medium. The writer has made a long series of experiments, extending from 1874 till the present time, and where mercuric oxide is used these two types of varnishes have given the best results. During this series of experiments it was found that if mercury in the metallic state was diffused through a paint in a very fine state of division, a much more trustworthy result could be obtained, as the metallic mercury dissolved so very slowly that a moderate quantity would last with good anti-fouling effect for a period of fifteen months. But the great difficulty lay in getting the finely-divided mercury to remain diffused through the liquid medium. It invariably settled to the bottom of the vessel, and the minute particles coalesced into large liquid globules of no use in painting. The following expedient was then hit upon. A mixture was made up containing very finely divided metallic zinc (obtained by distilling zinc into a chamber from which oxygen has been expelled and allowing the fumes to settle like flowers of sulphur) and oxide of mercury, together with the requisite pigments to form a coloured paint. This was made up in a very soft varnish, principally composed of resin and naphtha, and applied to the ship. The metallic zinc exerted a very efficient anti-corrosive action by rendering the iron negative, but it played another part. As soon as the mercuric oxide became soluble it electrolytically coated each little particle of exposed zinc with mercury, and as the zinc corroded away under the action of sea-water, finely powdered metallic mercury was left imbedded in the surface of the paint. The soft nature of the varnish caused

the surface to be constantly renewed, so that there was a regular supply of the anti-fouling substance. This has been found to be the most efficient anti-fouling composition as yet introduced, and has been approved of by the Admiralty for use in the Navy.

The conditions under which ships are painted, wet rough surfaces in winter and dry surfaces in summer, render it difficult to ensure uniform success with the same composition. In winter it dries too slowly, in summer too quickly, the former rendering it too soft when put in the water, the latter too hard. To obtain perfect results recourse would need to be had to compositions varied to suit the conditions, but of course in commercial practice this is almost impossible.

J. B. H.

**ANTI-FOULING PAINTS.** Pickering and Saale have patented (Eng. Pat. 10,457, 1884) a composition composed of barium carbonate, barium arsenite, powdered oyster shells, zinc oxide, red lead, quadroxalate of potash, and mercuric oxide or sugar of lead. These ingredients are ground together in the dry state and afterwards incorporated in a mixture of shellac dissolved in methylated spirits, and rosin, boiled linseed oil, turpentine, and spirits of tar (S. C. I. 3, 644).

Layden and McLean (Eng. Pat. 4,796, 1884) make a composition containing gold bronze powder 1 part, gum catechu 5 parts, teak varnish 7 parts, Schweinfurt or Vienna green 3 parts, yellow rosin, 15 parts, benzolene 30 parts, Stockholm tar 5 parts, black varnish 6 parts, Prussian blue 3 parts, colouring matter 37 parts (S. C. I. 4, 289).

Gisborne's composition (Eng. Pat. 312, 1885) contains mercury 10 lbs., litharge 9 lbs., blende, white or red lead or other like materials 14 lbs. chalk 15 lbs., and boiled oil (S. C. I. 5, 102).

Dennison's patent (Eng. Pat. 4,415, 1885) is for a mixture of 10 parts paraffin scale, 7 parts white lead, or other paint, 6 parts bronze green, 1 part light green, 2 parts rosin, 2 parts of arsenic, or cyanide or oxide of mercury.

Pointon (Eng. Pat. 13, 159, 1886) claims a paint or mixture of ground glass, pulverised slag or sand, linseed oil and crude turpentine in spirits of turpentine (S. C. I. 5, 540).

These paints are principally to be used for the bottoms of ships.

**ANTI-INCORUSTATORS.** This term is applied to various substances and mixtures used to prevent the deposition of scale in steam boilers. Nivet (J. Fab. Suc. 1882; S. C. I. 1, 428) shows that the conditions to be fulfilled by an anti-incrustator are (1) projections other than the roughness of the sides of the boiler on which the insoluble salts may crystallise must be offered; (2) the quantity used must not be so large as to materially increase the solid constituents and so raise the density of the water; (3) it must not be acid and (4) it must act both chemically and mechanically.

A great variety of substances have been patented as scale preventives, but Macadam (S. C. I. 2, 12) divides them into four divisions: (1) saline, (2) fats and oils, (3) paraffine and paraffine products, (4) other organic substances. The most common ingredient in the saline anti-incrustators is soda ash or the purer soda crystals;



sulphites, he states, seem to work well in boilers where sea-water is used; barium chloride he considers an undesirable constituent, as the barium sulphate formed sinks to the bottom of the boiler and adds to the scale. Tallow and oils, too, are objectionable, as they undergo decomposition, and the fatty acids attack the fittings of the boilers. Paraffin oil, free from paraffin scale, is very useful, but its action is purely mechanical. Peat, moss, and potatoes have also been found to act well. Substances containing tannin are used in several scale preventives, but as they are generally sold in a dry state they should be well soaked in water before being introduced into the boiler, otherwise they are liable to be carried over by the steam and give much annoyance by choking the pipes and valves. They are objectionable also in works where steam is to be blown into tanks for heating purposes, as in flax or hemp boiling, as the tannin carried over may cause stains. Zinc seems to be a good anti-incrustator for sea-water.

Details of the compositions of various anti-incrustators may be found in S. C. I. 1, 177, 219, 311, 338, 348, 487; 2, 12; 3, 101, 368, 434; 4, 105, 198, 484; 5, 94, 454; C. S. [2] 46, 1,087; and W. J. 22, 839; 29, 1,030.

**ANTIMONITE.** Native antimony sulphide *v.* **ANTIMONY.**

**ANTIMONY.** *Antimoine*, Fr.; *Antimon*, Ger. *Stibium*. Symbol, Sb. At. wt. 119.6 (Berzelius, Schneider, Cooke, Rose, Weber); 121.8 (Dumas, Dexter, Kessler).

*Occurrence.*—Antimony occurs native in small quantities, occasionally in rhombohedral crystals, at Andreasberg in the Hartz, Przibram in Bohemia, Sala in Sweden, Allemont in France, in the United States, New South Wales, and Quebec. It occurs in large masses in Sarawak, Borneo.

Combined with oxygen as the sesquioxide  $Sb_2O_3$ , it occurs in *antimony bloom*, *white antimony*, or *valentinite*, and in *senarmontite*, being found in workable quantities in the Algerian province of Constantine. In *antimony ochre* or *cervantite*, and in *stibiconite* and *volgerite* it occurs as antimonite of antimony  $Sb_2O_3$ .

Combined with sulphur it occurs as *stibnite*, *antimonite*, or *grey antimony ore*  $Sb_2S_3$ . In union with sulphur and oxygen together it forms *red antimony*, *antimony blende* or *kermesite*  $Sb_2O_3 \cdot 2Sb_2S_3$ .

Some antimony sulphides have recently been discovered which contain from 1.5 to 2.5 oz. of gold to the ton, but notwithstanding many proposed and patented processes, none is known by which the gold can be extracted profitably on a commercial scale.

With arsenic, antimony is found in *allemontite* or *arsenical antimony*. With silver in *diserisite*.

With sulphur and metals, antimony forms a number of *sulphantimonites*, among which may be mentioned *zinkenite*, *jamesonite*, *boulangerite*, and *feather ore*, containing antimony, sulphur, and lead; *niargyrite*, *pyrargyrite*, and *stephanite*, containing silver; *berthierite*, containing iron, and *antimonial copper glance*. Antimony is found in certain ferruginous waters.

Antimony ores occur in workable quantities in Mexico, California, North America, Canada,

Australia, Japan, Borneo, Cape of Good Hope, New Zealand, Asia Minor, Algiers, Italy, Spain, Portugal, Corsica, and Sardinia. Deposits of antimony sulphide have been discovered in Cornwall, Cumberland, and Scotland.

The veins in which antimony sulphide is found are usually from 4 to 6 inches in width, the ore being so mixed with gangue that it can only be separated by the costly processes of washing or hand-picking, or by lixiviation. It is occasionally found in 'pockets,' in which case it is usually of great purity.

By far the most general ore of antimony is the sulphide, but in some cases, as in Algeria, the oxide is found in workable quantities, and in other cases both oxide and sulphide occur together.

*Extraction.*—Metallic antimony is generally prepared from the native sulphide which occurs in a gangue of gneiss, porphyry, or other of the older rocks. From the gangue, the sulphide may be separated by a process of *lixivation*. Poor ores cannot, however, be treated in this manner as the lixivated residues contain from 10 to 25 p.c. of antimony.

The following method of lixiviation was formerly used where fuel is plentiful, as at Malbosc, in the Department of Ardèche, Wolfsberg in the Hartz, and in Hungary. The ore was placed in small lumps in a number of conical pots of 45 kilos. capacity, each perforated below and standing on a perforated plate over a sunken receiver. The pots were surrounded by fuel which continued to burn for 10 hours, the melted sulphide collecting in the receivers.

At La Lincoln, Wolfsberg and Haute Loire the pots were contained in a reverberatory furnace. At Schmöllnitz, in Hungary, the melted sulphide ran through channels into receivers outside the furnace.

At Malbosc the pots are replaced by cylindrical tubes, perforated below and standing on similarly perforated plates above the receivers. Each cylinder has a capacity of 500 lbs. of ore, four being heated in one furnace. Each has a hole at the side, through which the residues are removed, these holes being closed during the heating. The receivers are of clay, or of iron coated with clay.

Very poor or waste ores are sometimes lixivated in the open hearth of a furnace without the use of pots or cylinders. The hearth is inclined, and has in one place a depression in which the product is received. The hearth is best made of one solid piece of soft weathered granite, but this is frequently replaced by an iron trough coated with well-pressed fireclay, standing free in the furnace and resting upon three iron wheels, which run on iron rails let into the brickwork, or it may be made simply of fire-brick.

Too great a heat should in all cases be avoided, antimony sulphide being volatile at a white heat. The lixivated sulphide is known in the trade as 'crude antimony,' and usually contains from 71 to 72 p.c. of antimony.

For the *reduction* of the sulphide to metal several processes have been adopted.

The sulphide may be mixed with half its weight of charcoal to prevent caking, and roasted at a gentle heat, the heat being gradually in-



creased, but not to melting, whereby large quantities of sulphurous acid, arsenious oxide, and antimonious oxide are evolved, the two latter being collected in flues. 20 p.c. of the antimony is stated to pass off in this operation, the greyish or red mass which remains consisting of antimony tetroxide containing about one-sixth of its weight of the trioxide and some sulphide. This residue, known as antimony ash, is mixed with 0.5 part of cream of tartar, or 1 part charcoal and 0.5 part of potash, or  $\frac{1}{2}$  part charcoal saturated with a concentrated solution of sodium carbonate, and fused in a covered crucible at a low red heat, and poured into a hot mould. 100 parts of sulphide yield 44 parts of antimony. The slag which rises above the metal consists of alkaline carbonate mixed with double sulphide of antimony and potassium or sodium with charcoal, and is known as *crocus of antimony*. The action of the charcoal in this reduction consists in the removal of the oxygen from the antimony oxide, producing metallic antimony, and in the reduction of a part of the alkali. The alkaline metal thus set free combines with the sulphur of a part of the antimonious sulphide, freeing an equivalent quantity of the antimony and forming a double sulphide of antimony and potassium with a further quantity of the sulphide.

The sulphide may also be reduced by fusing 8 parts of sulphide with 6 parts of cream of tartar in a crucible heated nearly to redness, then adding 2 or 3 parts of potassium nitrate and fusing until perfectly liquid; or 8 parts of sulphide are mixed with 6 parts of cream of tartar and 3 parts of nitre, and are thrown in portions into a red-hot crucible and heated until perfectly fluid. By quietly fusing, with frequent stirring to prevent frothing, a mixture of 8 parts sulphide, 1 part sodium carbonate, and 1 part charcoal, 66 p.c. of metal is said to be obtained from the sulphide.

The antimony may also be reduced from the sulphide by fusion with iron scales or nails, which form a difficultly fusible iron sulphide. With rich ores iron in combining proportion is used. When these contain oxide as well as sulphide, a mixture of scrap iron and carbon is required. To poor ores a considerable quantity of sodium carbonate must be added to render the slag sufficiently fusible to permit separation of the metal. Liebig has recommended the addition of dry sodium sulphate to the mixture of iron and carbon.

Antimony prepared by these processes may contain sulphur, potassium, sodium, arsenic, lead, iron (especially when reduced by iron), and copper.

The annual consumption of antimony throughout the world is probably under 3,000 tons. Nearly the whole of this is smelted and refined in England by a crucible process in which iron is the reducing agent. The ores received in England vary considerably in richness.

On account of the great volatility of antimony and consequent waste in smelting no process has yet been devised for profitably working antimony ores containing less than 25 p.c. of antimony; in fact it is not found profitable to smelt ores containing much less than 50 p.c.; a good rich quality of ore (sulphide) contains from 65 p.c. to 68 p.c. of antimony.

Two forms of furnace are adopted. Where gas or other coke is near and cheap, the 'pot hole' furnace is used. This consists of a long row or nest of single 'pot holes' heated with coke, each crucible having its own pot hole or furnace. Two sets are usually built back to back, with a long flue running full length down the centre. Two workmen take charge of 8 or 10 pot holes.

Where a good hot flaming coal is cheaply attainable a form of flue furnace is preferred, which may be built a little below ground or raised above ground. The crucibles being placed a little apart, the furnace is fired and the flame is made to play in, and around, and between the crucibles. When the furnace is built below ground the crucibles are 'lifted' by the workmen from the top, but when raised above ground they are removed with round tongs from the side of the furnace.

The ore, of which the composition has been determined by analysis, is subjected to three operations:—

*Singling.* About 40 lbs. of the sulphide in pieces half the size of an egg is introduced with a quantity of the slag produced in 'doubling' (*v. infra*) into a red-hot plumbago crucible. Above this is placed a quantity of old iron and tinplate, beaten into a conical form; with ore containing 50 to 55 p.c. of antimony, 20 lbs. of this would be used. When the charge has melted, the iron is pressed into the mass, reducing it, setting free metallic antimony and forming a slag of iron sulphide. The crucible is emptied, and after cooling, the antimony is removed from below the slag. The slag of iron which was formerly a waste product is now used as a cheap source of sulphuretted hydrogen for the precipitation of arsenic from sulphuric acid made from Spanish pyrites.

*Doubling.* The buttons or 'singles' from the first melting are sorted so that those which contain an excess of sulphur may be melted with those containing an excess of iron; 70 or 80 lbs. of these, together with 2 lbs. of salt cake and a small quantity of 'star metal' slag, are melted in a crucible for 1 to  $1\frac{1}{2}$  hours and poured into a cast-iron bowl with the formation of 'bowl metal.'

*Refining, frenching, or melting for 'star metal.'* About 60 or 70 lbs. of 'bowl metal,' with a pound or two of American potashes, and about 10 lbs. of the star metal slag broken into small fragments, are placed in a red-hot crucible and stirred with an iron rod, the workman judging from the slag adhering to the rod when the refining is completed; less than one hour is usually required.

When refined, the metal is poured into moulds, carefully covered with slag and left undisturbed to allow of the formation of the crystalline structure. The refined star metal still contains arsenic and sulphur.

The refining of the metal first run from the ore is an operation requiring practical skill and technical knowledge, as the buyer demands a very high degree of purity in the metal.

Unlike many other metals, antimony carries on its face its own character for purity. When 'pure' a beautiful fern leaf or 'star' appears upon its surface, and according to the length and form of this 'star' on the ingot its quality

is determined. The presence of a relatively small percentage of impurities in the metal will prevent it from 'starring.' It is this peculiar characteristic of pure antimony to crystallise on the ingot in the fern leaf or star form when cooling which originates the trade term of 'star antimony' for good quality of antimony.

The sulphide may also be reduced on the hearth of the furnace already described. The partly roasted ore, which contains the sulphide and oxides of antimony, is mixed and fused with 8 to 13 p.c. coal and 9 to 11 p.c. of soda, frequently with the addition of iron, in which case the slag produced is much less fusible and does not entirely cover the bath of metal; the antimony produced also contains much iron (D. P. J. 162, 449). Where carbonate of soda is used for the fusion the mass froths considerably and attacks the furnace hearth.

The following analyses show the composition of crude antimony, I. and II. being metal made with scrap iron, the arsenic and gold being due to admixed pyrites; III. and IV. metal from roasted ore smelted in a blast furnace (D. P. J. 1883, 250, 123; R. Helmhaecker, Berg. u. Hütt. Zeit. 1883, 191).

	I.	II.	III.	IV.
Antimony .	94.5	84.0	97.2	95.0
Iron .	3.0	10.0	2.5	4.0
Sulphur .	2.0	5.0	0.2	0.75
Arsenic .	0.25	1.0	0.1	0.25
Gold .	traces	—	—	—

At the newly erected works at Bányá, Hungary, the ore principally worked is the sulphide, containing about 50 p.c. antimony; a small quantity of the native oxide is also worked. The residues from the liqation of the ore contain from 21 to 25 p.c. of antimony; they are roasted on a bed of wood in a kiln for 6 or 7 weeks, and then smelted in a blast furnace with 20 p.c. coke or charcoal (*v.* Balling, Chem. Zeit. 9, 1,825 and 10, 1,198-1,199). By fusing on the small scale in a wind furnace 5 kilos. liqation residues containing about 14 p.c. antimony with 3 kilos. puddling slag, 2 kilos. soda and 25 kilos. wood charcoal, C. A. Hering has produced 0.56 kilos of clean metallic antimony (D. P. J. 230, 253-263).

Methods of treating antimony ores have also been proposed by which the antimony is converted into the volatile chloride, as in Lyte's process of roasting the ore with salt. The ore may also be subjected to the action of hydrochloric acid gas in a reverberatory or muffle furnace, the volatilised chloride being condensed in a solution of hydrochloric acid (D. P. J. 250, 79-88, and 123-133).

*Purification.*—Metallic antimony may be freed from sulphur, arsenic, copper, and iron (when not present in too great quantity), but not from lead, by fusing 16 parts of the coarsely powdered metal with 1 part sulphide of antimony (more being used when iron is present in greater excess) and 2 parts dry carbonate of soda, for one hour. The metal produced is again fused with  $1\frac{1}{2}$  parts of carbonate for one hour, and fused a third time with 1 part carbonate. 16 parts of impure antimony thus produce about 15 parts of the pure metal.

In this process the objectionable metals (except lead) in the antimony are converted into

sulphides and carried away into the slag, a part of the arsenic being also transformed into arsenate of soda. Care must be taken to prevent charcoal from entering the crucible, as the arsenic would then be reduced and would again render the antimony impure (Liebig). The antimony also contains sodium (Anthon, Repert. 59, 240), which may be removed by digestion of the coarsely powdered antimony in water and subsequent fusion. Unless sufficient sulphide has been used to remove the whole of the iron the antimony will still contain arsenic (A. 29, 58; Handwört. 2te Aufl. II. 45; also Buchner, Repert. 11, 267).

Duflos states that iron and copper can be removed by fusion with  $\frac{1}{2}$  part of nitre (Br. Arch. 36, 277, and 38, 158). Berzelius removes potassium, sodium, arsenic, and iron by fusion with  $\frac{1}{2}$  to 1 part of antimonious oxide.

According to R. Helmhaecker (Berg. u. Hütt. Zeit. 1883, 191, and D. P. J. 250, 123), the following process has been adopted for the purification in Bohemia: A 'glass of antimony' is prepared by fusing a mixture of the crystalline antimony oxide which collects on the hotter portions of the flues with sulphide of antimony, until it forms a glassy dark grey or brown mass; this is mixed with the carbonate for the purification of the metal, and is occasionally used alone where the metal is but slightly impure.

The bed of the furnace is heated to a cherry red and 600 to 700 kilos. of crude antimony placed on it; a quantity of oxide and some arsenic escape, and in from 30 to 60 minutes the metal has run down. From 3 to 7 p.c. (according to the purity of the metal) of carbonate of soda, sometimes mixed with coal or coke, is then added. The metal is thus covered and fumes less, small jets of flame appearing occasionally on its surface; the temperature is raised, the metal remaining under the slag for from 1 to 3 hours (determined by the workman), the slag then becomes thick and is removed by drawing it through the door with a long handled flat transverse iron.

Three p.c. of antimony sulphide and  $1\frac{1}{2}$  p.c. of oxide are then thrown on the surface of the metal, and when melted,  $4\frac{1}{2}$  p.c. carbonate of potash or of a mixture of carbonate of potash and soda, are added. By this means the iron and last traces of sulphur are removed; in less than 15 minutes the refining is complete and the critical operation of lading is performed. A cast-iron hemispherical ladle holding 15 to 20 kilos is riveted to a chain hanging from the roof exactly in front of the working door, before which the cast-iron moulds for receiving the metal are arranged on a stoue table. The workman dips his ladle obliquely, removing some slag with the metal; part of this is first poured into the mould to prevent the metal from actually touching the mould, and the metal is well covered with the slag and left at rest. Unless this be done the 'starring' will be imperfect, and, as this is considered a test of purity, its value will be lowered in the market. The slag may generally be used again. The oxide which condenses in the flues is removed as seldom as possible, being, as well as the furnace work, very injurious to the operators.

The cost of refining 100 kilos. of regulus is from 4 to 5 shillings.

For pharmaceutical purposes it is important to prepare antimony quite free from arsenic. This may be accomplished by Wöhler's method. A mixture of 4 parts powdered commercial antimony, 5 parts sodium nitrate, and 2 parts sodium carbonate (to prevent the formation of insoluble arsenate of antimony) is thrown into a red-hot crucible. Combustion takes place quietly, the mass is pressed together and more strongly heated for half an hour, so as to become pasty without fusion, being pressed down as it rises from evolution of gas. While still hot and soft it is removed, reduced to powder and boiled with frequent stirring in water, the finer powder is poured off with the water, and the residue again treated, the washings being mixed with that first obtained. The water, which contains the whole of the arsenic but no antimony (Meyer) is removed from the insoluble portion by subsidence, decantation, and filtration. The residue of sodium antimonate should be white, but the presence of lead imparts a yellow colour. It is dried and fused with half its weight of cream of tartar at a moderate heat, cooled, broken into small lumps, and the potassium and sodium removed by digestion in water. The powdered metal is then fused into a button.

This method may be used quantitatively for the separation of antimony from arsenic. If the sodium nitrate be replaced by potassium nitrate a portion of the antimony will enter into solution with the arsenic as potassium antimonate (v. C. Meyer, A. 46, 236; C. C. 1,348, 828). Arsenic may also be completely removed by fusing the antimony in succession with 1st, potassium carbonate; 2nd, potassium nitrate; 3rd, antimonie oxide; 4th, potassium carbonate (Th. Martins, Kastn. Arch. 24, 253), or by fusing three times with fresh portions of sodium or potassium nitrate.

Duflos (Kastn. Arch. 19, 56) recommends a process in which the arsenic is driven off as fluoride by means of sulphuric acid and fluor spar. (See further Schw. 42, 501, also Buchner and Herberger, Repert. 38, 381, 256.)

Pure antimony may be obtained by heating tartar emetic to low redness and digesting the resultant mass in water to remove the potassium. The powder thus obtained may then be dried and fused into a button.

#### *Tests for impurities in antimony.*

**Sulphur.** The powdered metal evolves sulphuretted hydrogen gas (which blackens lead paper) on heating with strong hydrochloric acid.

**Potassium or sodium.** The metal is greyish and loses its lustre on exposure to air; it has an alkaline taste and reaction, and evolves hydrogen on immersion in water.

**Arsenic.** If deflagrated with  $\frac{1}{2}$  its weight of sodium nitrate, boiled with water and filtered, the arsenic enters into solution leaving the antimony behind; the solution is saturated with sulphuretted hydrogen (if an orange precipitate, consisting of antimony sulphide, falls this must be filtered quickly, it is due to the presence of a trace of antimony in the solution). The arsenic is deposited as the lemon yellow sulphide on standing.

**Lead and copper.** The metal is powdered and treated with dilute nitric acid, evaporated nearly to dryness, taken up with water and filtered; the addition of sulphuric acid precipitates white lead sulphate, and the addition to the filtrate of potassium ferrocyanide gives a brown precipitate in presence of copper.

If sulphur as well as lead be present in the antimony the lead is converted at once into sulphate by the action of nitric acid, the residue on evaporation is digested with yellow ammonium sulphide, which dissolves the antimonie oxide and leaves black lead sulphide.

**Iron.** The powdered metal is ignited with three parts nitre and washed with boiling water, the residue is boiled with hot dilute hydrochloric acid; on the addition of potassium ferrocyanide a blue precipitate is produced.

When antimony containing arsenic and iron is heated on charcoal it gives a garlic odour and becomes coated with oxide of iron; it ceases to burn on removal of the flame and yields a dull surface and yellow oxide (Liebig). The pure metal under such circumstances burns brilliantly and becomes coated on cooling with white crystals of the oxide.

**Detection and estimation.**—When fused on charcoal with potassium cyanide or sodium carbonate or a mixture of the two, antimonial compounds produce a brittle white bead of metallic antimony with white fumes and a white incrustation on the charcoal; the bead leaves a white residue on treatment with nitric acid, which is soluble in cream of tartar or tartaric acid. Sulphide of antimony melts readily in the candle flame.

In valuing ores containing the sulphide the ore is broken into pieces about  $\frac{1}{2}$  to 1 inch diameter, and from 2,000 to 7,000 grains of the lumps (avoiding dust), according to the probable richness of the ore, are selected. A Hessian crucible with a hole at the bottom covered with a piece of charcoal, is placed within another crucible of such size that the upper one enters about one inch. The ore mixed with charcoal of about equal quantity and size is placed in the upper crucible, covered with a layer of charcoal and luted down. Heat is then applied, the lower crucible being below the furnace bars and surrounded by ashes to keep it cool. The heat should be maintained at a cherry red, but not higher, for from 1 to 1½ hours. On cooling, the regulus is removed from the lower crucible and weighed. It should be well fused, bluish grey, and of bright fibrous crystalline fracture, the residue in the upper crucible should be examined to see if it is free from visible sulphide. As the sulphide contains 71.76 p.c. of antimony, the percentage of antimony in the ore may be roughly calculated, but it is preferable to treat it by the following process, which may be used for any sulphide or very rich ore.

From 100 to 300 grains of the powdered sulphide or ore is roasted at a low temperature in a roasting dish (scorifier) with constant stirring, especially at first, to complete the oxidation of the whole; otherwise, especially if the temperature be too high, some antimony vapour will escape. The resultant oxide is quite non-volatile. The whole of the grey or greyish-white product is mixed with 300 to 500 grains sodium carbo-



nate and 20 to 50 grains charcoal powder, placed in a crucible and gradually heated to redness (twenty to thirty minutes being allowed for this), and when tranquil poured into a mould, and the button of metal cleaned and weighed. Instead of carbonate and charcoal, the ore may be mixed with 1 to 3 parts black flux and  $\frac{1}{4}$  part borax, covered with a layer of salt, and treated as above. This method, with the omission of the roasting, may be used for assaying the oxides of antimony.

To obtain the exact percentage of antimony the ore or metal is dissolved in strong hydrochloric acid containing a small quantity of nitric acid, and the solution diluted with water. If it becomes turbid, hydrochloric or tartaric acid is added, and the solution filtered, saturated with sulphuretted hydrogen gas, boiled until the gas ceases to be evolved, filtered, and the precipitate dried. The precipitate, with the filter paper, is placed in a basin and covered with a funnel, and *fuming* nitric acid added, the funnel being slightly raised. At first the action is violent; on subsiding, the mass is digested for about twenty minutes, when the antimony will have been oxidised to the antimonie anhydride and the sulphur to sulphuric acid. If other than *fuming* nitric acid be used, the sulphur is liable to form small globules, which are difficult to oxidise. The white residue is evaporated nearly to dryness and washed on a filter until free from acid, dried, ignited strongly, and weighed as the tetroxide  $\text{Sb}_2\text{O}_4$ , which contains 79.22 p.c. of antimony.

#### *Properties of antimony.*

Antimony is a brilliant, bluish-white, brittle crystalline metal of specific gravity 6.716 to 6.86. It melts at  $450^\circ\text{C}$ ., and boils at a white heat, burning in air, or slowly distilling in an atmosphere of hydrogen.

Its crystalline structure may be seen by melting in a crucible, suffering a crust to form and crystallisation to commence at the sides, and pouring out the still liquid portion; rhombohedral crystals are thus obtained. *Pure* antimony crystallises only with difficulty (Cooke and Matthiessen).

Antimony expands on solidifying, and imparts this property to its alloys. (Duflos states that *pure* antimony does not expand on solidifying.) It is a bad conductor of heat and electricity. At the ordinary temperature it is not acted on by the air, but oxidises quickly on melting, and burns at a red heat, producing white fumes of the trioxide. It is oxidised by nitric acid of various strengths, dilute acid producing principally the trioxide, and the concentrated acid producing the pentoxide (H. Rose, *Analyt. Chem.* 1, 258). Dilute sulphuric and hydrochloric acids are without action on it, but the strong acids produce the sulphate and chloride respectively. When fused with borax or other vitrifying material it imparts to them a yellow colour.

Powdered antimony ignites when thrown into chlorine or bromine vapour, and floats in liquid globules on liquid bromine, being converted into the chloride and bromide respectively; it also combines, but less energetically, with iodine.

Antimony is precipitated as a fine powder by the action of zinc on an acid solution of an

antimony salt. In this form it is sold as 'iron black' for producing an appearance of polished steel on papier maché, plaster of Paris, and zinc ornaments.

Brass can be covered with a fine lustrous coating of antimony by dipping in a hot mixture of 1 part tartar emetic, 1 part tartaric acid, 3 or 4 parts powdered antimony, 3 or 4 parts hydrochloric acid, and 3 parts water.

It may be deposited electrolytically on brass or copper by using a bath of the double chloride of antimony and ammonia acidulated with hydrochloric acid.

Antimony occurs in two modifications—(1) The crystalline or ordinary form; (2) The amorphous or explosive form. Both of these can be obtained by electrolysis. The amorphous form is best prepared by the action of a weak constant electric current on a concentrated acid solution of antimony trichloride, the strength of current bearing a constant relation to the surface of deposition, not less than  $\frac{1}{2}$  grain being deposited per square inch per hour. Thus produced it is bright and steel-like in appearance, with an amorphous fracture and specific gravity 5.78. When heated above  $77^\circ\text{C}$ ., or struck or scratched, it rapidly changes into the crystalline form, increasing in density, with the production of great heat. Antimony trichloride is always contained in the metal to the extent of 4.8 to 7.9 p.c., and is given off when the form changes. This may be held mechanically by the metal; but Gore regards the explosive form as an unstable compound of varying proportions of metallic antimony and a salt of antimony. Böttger states that occluded hydrogen is contained in the metal (C. C. 1875, 674); but Pfeifer (A. 1882, 209, 162-184) has been unable to confirm this statement.

#### *Alloys of antimony.*

Antimony alloys with most of the heavy metals and with the alkaline metals. It generally increases the fusibility, brittleness, and hardness of the metals with which it is combined, and imparts the valuable property of expanding on solidification, thus producing very fine impressions. The alloys of silver, gold, and lead with antimony have a greater density than the mean of the constituents, while those of iron, tin, and zinc are of diminished density. The sharpest impressions are produced when any of these alloys are cast at a low temperature (S. C. I. 1, 982).

With Lead antimony mixes readily in all proportions. By the addition of antimony to red-hot lead, alloys which crystallise in rhombohedra have been obtained by F. de Jussieu (C. R. 38, 1321-1322). An alloy of equal parts of lead and antimony is very brittle, and rings when struck. Nasmyth has recommended the addition of 5 p.c. antimony to lead for use instead of bronze in taking casts of works of art (*Athenæum*, No. 1176, 511). Type metal consists of lead and antimony, with the addition, frequently, of tin or bismuth. Common type contains 100 lead to from 17 to 20 antimony; that used in Germany usually contains 15 p.c. antimony. For finer and especially small type tin is added; such type-metal may contain fine lead (tea lead) 75, antimony 20, block tin 5; or fine lead 70, antimony 25, block tin 5; or lead 2, antimony 1, tin 1.

Stereotype plates contain fine lead 112, antimony 18, block tin 3. Music plates have the same composition.

Wetterstedt's patent ship sheathing consists of 100 lead to about 3 antimony, but does not appear to have been used to any extent. The alloy, containing varying proportions of antimony, is also used in lead pipes, for making pumps and taps for raising acid in alkali works, in the manufacture of cannon balls and shot, and for the emery wheels and tools of the lapidary.

Tin forms numerous useful alloys with antimony, especially with the addition of other metals. Common Britannia metal consists of tin 140, copper 3, antimony 9. Britannia metal for castings: tin 210, copper 4, antimony 12; ditto for lamps: tin 300, copper 4, antimony 15. The best Britannia metal contains tin 90, antimony 10; lead and bismuth being carefully excluded. Copper also is never added except for the production of colour. The exact proportion of antimony used depends on the quality of the tin, and is always ascertained experimentally. The presence of arsenic in the antimony diminishes the ductility of the product (*v. BRITANNIA METAL*). Superior pewter is made by fusing together tin 12, copper 1, antimony 1.

*Metal argentum* contains tin 85.5, antimony 14.5.

*Ashbury metal*: tin 77.8, zinc 2.8, antimony 19.4. Ships' nails, tin 3, lead 2, antimony 1.

The alloys of tin and antimony are much used for machine bearings, especially with the addition of copper and occasionally lead. Those containing copper are used for railway axles, rings and collars for machinery, the bearings for screw propellers, &c., in preference to gun metal, the friction being much diminished. For the bearings of locomotive and other axles the following antifriction metals are used:—

	Copper	Antimony	Tin	Lead
At Crewe works . . .	5.3	10.5	84.2	—
For German locomotives. . .	5.0	10.0	85.0	—
Babbitt's metal . . .	1.5	13.0	45.5	40.0

Where the pressure on the bearing is very great the metal used may contain copper 20, tin 4, antimony 0.5, lead 0.25.

**Copper.** The presence of 0.15 p.c. of antimony renders copper both cold and hot short. With varying proportions of the two metals, shades from pure copper-red to rose-red, crimson, and violet may be obtained, the last when equality is reached. Two definite compounds of copper and antimony appear to exist, viz.  $\text{SbCu}_2$ , a violet alloy known as 'Regulus of Venus,' and  $\text{SbCu}$ , (Kamensky, P. M. [5] 17, 270; v. also Ball, C. J. 1888, 167).

Antimony is frequently added to heighten the colour of brass. These alloys are harder and finer in texture than copper or brass, and take a better polish. Antimony is frequently added for this reason to the material for concave mirrors. It is also added occasionally to bell metal, as it is believed to add to the intensity and clearness of the sound. Many celebrated old bells contain antimony, e.g. 'Old Tom' of Lincoln which contains about 0.03 p.c.

**Zinc.** Antimony forms definite crystalline compounds with zinc, which, however, differ

widely in composition while retaining the same form; they decompose water rapidly at the boiling temperature.

Iron containing less than  $\frac{1}{4}$  p.c. of antimony is both hot and cold short. A mixture of 7 parts antimony and 3 parts iron heated to whiteness with charcoal forms a hard white alloy which strikes sparks with steel.

Melted gold absorbs the vapour of antimony, but gives it up almost entirely on further heating. Gold loses its malleability when  $\frac{1}{2,000}$  of antimony is present. An alloy of 9 gold and 1 antimony is white and very brittle, with an amorphous porcelain-like fracture. Silver antimonide occurs as the mineral *diserasite*.

#### COMPOUNDS OF ANTIMONY.

The principal compounds of antimony are formed by combination with oxygen, sulphur, and chlorine; some compounds contain two of these negative elements, of which the oxychloride or *powder of Algaroth*, and the oxysulphide or glass of antimony are examples.

The most important of these are the trichloride, trisulphide, and trioxide.

**Antimony trisulphide**  $\text{Sb}_2\text{S}_3$ .

*Crude antimony, antimony ore, sesquisulphide of antimony; Schwefelspiessglanz; Grauspiessglanzerz; Stibium sulphuratum nigrum; lupus metallorum.*

This substance, as it occurs naturally, or after liquation, is usually too impure to be employed for other purposes than the preparation of the metal.

The ordinary sulphide may be prepared by the following methods:—

(1) Thirteen parts pure antimony are mixed with 5 parts flowers of sulphur, and projected in portions into a red-hot crucible; when completely fused it is poured out and any free metal detached.

(2) Sulphuretted hydrogen precipitates it as an orange precipitate from a solution of an antimony salt.

(3) Digest for two hours in a closed vessel 1 part crude antimony sulphide, 1 part pearl ash,  $1\frac{1}{2}$  parts lime, and 15 parts water, and add sulphuric acid; the alkaline sulpho-salt first formed is decomposed by the acid with the precipitation of the pure sulphide. Antimony sulphide is soluble in alkaline sulphides and in acid potassium sulphate. When finely powdered and rubbed to a paste at 20° or 30°C. with strong sodium sulphide solution a coppery metallic mass is produced, and the liquor on addition of more sodium sulphide yields Schlippe's salt.

The sulphide is used to some extent in refining gold from silver and copper, and in the preparation of safety matches and percussion pellets for cartridges, in pyrotechny and in veterinary surgery.

**Kermes mineral.** *Brown-red antimony sulphide. Pulvis Carthusianorum. Sulph. stibiatum rubrum.*

Kermes mineral usually consists of a mixture of the trisulphide and trioxide containing alkali. Berzelius and Rose state that some samples examined by them consisted of a true double sulphide of potash and antimony.



*Preparation.*—Fuchs asserts that if antimony sulphide is heated and *suddenly* cooled in water it yields an orange-red, less dense powder of kermes. A. Ditte (C. R. 102, 212) does not confirm this statement.

(1) Four parts pure potassium carbonate and 11 parts pure antimony sulphide are heated to fusion in a covered crucible, cooled, boiled with water, and filtered. The solution on exposure to the air deposits kermes, the residue from the first boiling is heated with the mother liquor from some previously deposited kermes, and yields a further quantity; this operation is repeated until an insoluble residue of trisulphide and trioxide is left. Each successive deposit of the kermes contains a larger amount of the oxide.

(2) Fuse together 2 antimony, 1 sulphur, and 3 sodium carbonate; or, 1 antimony sulphide and 3 or 4 tartaric acid until fumes cease to be evolved, and treat the product as in (1).

(3) The slags from the reduction of antimony ore with cream of tartar slowly precipitate kermes when treated with water; this is sold to veterinary surgeons as 'kermes by the dry way.' When antimony sulphide is boiled with potash and precipitated with an acid the kermes produced contains no oxide (Liebig). The kermes produced by the action of *dilute* alkaline carbonate on antimony sulphide also contains no oxide (Rose). The oxide may be removed from ordinary kermes by digestion with tartaric acid. A solution containing so much alkali as to give no precipitate on cooling gives, when treated with carbonic acid gas, a highly sulphurated kermes containing antimony pentasulphide.

Kermes is a brown-red, loosely coherent powder, with a brown streak, containing water which is given off below 100°C. It is lighter than the ordinary sulphide. The kermes containing antimony oxide, when fused and solidified, is destitute of crystalline structure, while that free from oxide produces a highly crystalline solid.

*Antimony pentasulphide*  $\text{Sb}_2\text{S}_5$ . *Golden sulphide of antimony; sulphur antimonii auratum.* Prepared by boiling the trisulphide with potash and ground sulphur, filtering and precipitating with acid. Redwood recommends 4 parts black antimony sulphide, 8 lime, and 80 water, digested, filtered, and precipitated with hydrochloric acid; or, 2 sulphide, 4 potassium carbonate, and 1 sulphur, to be fused, treated with 20 parts water, filtered, and the solution precipitated with a large excess of sulphuric acid.

On treating the mother liquor from kermes mineral with an acid, the pentasulphide is precipitated with evolution of sulphuretted hydrogen. The mother liquor from Schlippe's salt also yields this substance on the addition of an acid (R. Bartley, C. J. 1876, 1, 748). It generally contains free sulphur.

Antimony pentasulphide combines with alkaline sulphides, forming sulphantimonates, which as well as the sulphantimonites (which contain less sulphur) are known as 'livers of antimony.' Of these the sodium sulphantimonate, or *Schlippe's salt*, is the most important.

A mixture of 11 parts finely powdered antimony trisulphide, 13 crystallised sodium car-

bonate, 1 flowers of sulphur, 5 recently slaked lime, and 20 water is digested at the ordinary temperature for twenty-four hours with frequent stirring, in a vessel which can be closed. It is then strained and washed several times with water, the solution and washings are evaporated in a porcelain or clean iron dish until a sample yields crystals on cooling; the solution is then cooled, and the resultant crystals washed with cold water and dried in the open air or in a desiccator at the ordinary temperature. The salt is more rapidly formed when the mixture is heated (Liebig, Handwörter. d. Chem., 2te Aufl. 2, 139). Also Gm. 4, 384.

Oxysulphides of antimony are formed by the combination of the sulphides and oxides or by the partial oxidation of the sulphides.

*Antimony crocus or saffron.* Fuse together 3 parts of antimony trioxide and 1 part trisulphide, or fuse the oxide with the calculated quantity of sulphur.

The scoria from the fusion of the sulphide with carbon and alkaline carbonate in the preparation of the metal is known as crocus of antimony.

Crocus of antimony is a brownish yellow body.

*Glass of antimony. Vitrum antimonii.* When antimony sulphide is fused until the necessary amount of sulphide has been converted into oxide, the whole forms a glassy mass of this compound. The best method of preparation is to roast the sulphide completely into oxide and fuse the product with  $\frac{2}{3}$ th part of sulphur. Its colour varies with the proportion of sulphur present from yellowish red to hyacinth red. The best quality is of a fine red colour and contains 8 antimonious oxide and 1 antimonious sulphide.

*Antimony cinnabar* is an oxysulphide of a fine vermilion colour, soft and velvety, and unaltered by air or light; it is used in the preparation of oil and water colours, and in calico printing. It is prepared by dissolving antimony oxide in hydrochloric acid, and placing the solution in a large wooden tub which is  $\frac{2}{3}$ ths filled with calcium hyposulphite. The mixture is stirred and heated with steam to 70°, the precipitate soon subsides as a yellowish sediment which changes to a bright orange red, and is thoroughly washed, and dried below 50°C. N. Teck (C. C., 26, 1880) prepared it from 4 parts tartar emetic, 3 tartaric acid, 18 water mixed at 60°C with hyposulphite of soda and heated to 90° (Wagner) or 4 volumes antimonious chloride of sp.gr. 1.19 mixed with 10 vols. water and 10 vols. hyposulphite of 1.19 sp.gr. and heated gradually to 55° (Mattieu Plessy).

*Antimony yellow (Mérimeé's yellow).* According to the method of Mérimeé a mixture of 3 parts bismuth, 24 parts antimony sulphide, and 64 parts nitre, is thrown little by little into a heated crucible, fused, powdered, washed, and dried. In this way bismuth antimonate is produced. Of this 1 part is mixed with 8 parts ammonium chloride and 128 parts litharge and fused as before. The time occupied and the temperature used cause considerable variations in the colour. Mérimeé's yellow is a fine permanent colour of good body. It is only used for the finest painting.



*Naples yellow* is essentially an antimonate of lead containing excess of lead oxide, but mixtures of carbonate and chromate of lead are also sold under the name. Many processes may be used for its preparation. According to Brunner, a mixture of 1 part tartar emetic, 2 parts lead nitrate, and 4 parts sodium chloride is heated, just to fusion, for two hours. The cooled mass is placed in water and soon falls to pieces. According to Guimet it may be produced by heating a mixture of 1 part potassium antimonate and 2 parts red lead. It is a fine very permanent orange or yellow pigment, used in oil painting and, mixed usually with a lead glass, for glass and porcelain staining.

**Antimony trichloride** (*Butter of antimony*).

Prepared by dissolving the sulphide in strong hydrochloric acid with a small quantity of nitric acid and evaporating to dryness.

To prepare the pure chloride, the acid solution is evaporated until it just crystallises on standing in a cool place; it is then transferred to a retort and distilled until a drop of the distillate solidifies on a cold surface, the receiver is then changed and the further distillate is pure.

It is a white, buttery, semivitreous, deliquescent solid, becoming oily at 72°C. and boiling at 200°C. It is used as a caustic in medicine, for the preparation of tartar emetic, and as a 'bronzing solution' for gun barrels &c. For this purpose a saturated solution is mixed with olive oil, rubbed over the warmed metal and exposed to the air until the proper colour is produced. When bronzed, the metal is polished with a burnisher or with wax, or coated with a varnish of 2 oz. shellac, 3 drachms dragon's blood, dissolved in 2 quarts of methylated spirit.

**Antimony oxychloride.** *Basic chloride*, powder of *Algaroth*; *pulvis Algarothi*; *S. Angelicus*; *mercurius vita*, &c.

Water is added to a solution of the trichloride until it is distinctly turbid when it is filtered (the precipitate carries down any traces of sulphuretted hydrogen which may be present, and which if left would soon turn the substance yellow). Five to ten volumes of water are added and the precipitate is washed with cold water and filtered. Its composition varies with the temperature at which it is produced and the amount of water used, varying between  $\text{SbOCl}$  and, where a very large amount of water has been used,  $\text{Sb}_2\text{O}_3$ . It is a white powder and is principally used for the preparation of pure antimonious oxide and tartar emetic.

**Antimonious oxide**  $\text{Sb}_2\text{O}_3$ . *Trioxide of antimony*. If antimony is powdered and heated in a shallow dish it eventually forms antimony tetroxide  $\text{Sb}_2\text{O}_4$ ; this, together with the unchanged metal, is fused in a crucible, when the tetroxide and antimony react, forming antimonious oxide, the excess of antimony sinking to the bottom of the crucible.

For pharmaceutical purposes the Dublin College advises that 20 parts of finely powdered antimony sulphide be gradually added to 100 parts hydrochloric acid containing 1 part nitric acid, and heated, gently at first, and then more strongly, until sulphuretted hydrogen ceases to be evolved. It is then boiled for one hour more, enough water is added to produce a slight pre-

cipitate, which removes the last traces of sulphuretted hydrogen, and filtered into a vessel containing 1 gallon of water, precipitating the oxychloride, which is filtered and washed until it ceases to have an acid reaction; it has then become converted into the trioxide.

It is a white fusible solid, slightly soluble in water, volatile at a red heat. It becomes further oxidised to the tetroxide  $\text{Sb}_2\text{O}_4$  on heating in air, and is then non-volatile.

In presence of alkalis it absorbs oxygen; for this reason it has been proposed to use it for reducing nitrobenzene to aniline, and in the preparation of aniline red.

It is used for the preparation of tartar emetic. When ground with linseed oil it is sometimes used as a substitute for white lead, being less injurious to the workmen and less acted upon by sulphur gases; it has, however, less 'body' and is more expensive.

**Tartar emetic.** *Potassium antimony tartrate. Tartarus stibiatus. Brechweinstein; spießglanzstein.*  $2\text{C}_6\text{H}_5\text{K}(\text{SbO})\text{O}_6\cdot\text{H}_2\text{O}$ . Three parts antimonious oxide and 4 cream of tartar are made into a thin paste with water and digested for about half an hour, keeping the water at constant volume; 8 parts of water are then added, boiled, and filtered while hot. The oxychloride or oxysulphide may be substituted for the oxide, but not so satisfactorily.

Tartar emetic forms octahedral crystals which give off a part of their water on exposure to the air. They dissolve in 14.5 parts cold and in 1.9 parts boiling water. They show an acid reaction with litmus, and have a nauseous metallic taste, 5-10 centigrams causing vomiting, and larger quantities being very poisonous.

It is used in medicine and in the preparation of pomades &c., and also largely as a mordant in dyeing and calico printing. Mixtures of tartar emetic for mordanting are sold containing as much as 33 to 59 p.c. zinc sulphate at a lower price, under the names *tartar emetic powder*, *tartar emetic substitute*, *antimony mordant*, &c. It is known that zinc acetate may partly replace the tartar emetic with advantage, but the sulphate appears to be a simple adulterant (*v. H. Smid, C. Z. 1882, 949*).

Several other compounds of antimony have been proposed instead of tartar emetic for mordants. E. Jacquet (*D. P. J. 257, 168*) advises the use of a mixture of basic antimony oxalate with twice its weight of ammonium oxalate. Nölting recommends the double oxalate of potash or of ammonia and antimony (*D. P. J. 255 [3] 122*). It is stated that the latter compounds have long been used under other names.

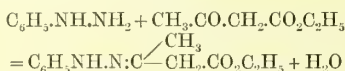
The use of the fluoride (which is not precipitated with excess of water) and the double fluorides of antimony and the alkalis has been patented by S. McLean. C. Watson, jun., has recently patented a process for using trichloride with sufficient common salt to prevent the precipitation of the oxychloride (*v. also G. Watson, S. C. I., 1886, 5, 591*; B. W. Gerland *S. C. I. 1884, 4, 643*; and Kopp and Bruère, *S. C. I. 1888, 566*). A double salt of antimony fluoride and ammonium sulphate  $\text{SbF}_3(\text{NH}_4)_2\text{SO}_4$  known as 'antimony salts' is also used in dyeing, but as it attacks glass as well as metal, it should be stored and worked in wooden vessels.

A good bath is 100 litres water, 400 grams antimony salts, 200 grams soda crystals at a temperature of 50° (Frey. Bull. Soc. Md. Mulhouse, 1888, 301).

**ANTIMONY OCHRE.** A mineral found in Servier Co., Arkansas. Hardness a little over 4. sp.gr. 5.58. Contains 76.15 p.c. Sb, 19.85 O, 3.08 H<sub>2</sub>O, 0.92 SiO<sub>2</sub> (Santos, C. N. 36, 16).

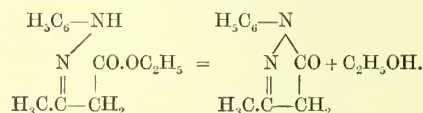
**ANTIMONY SALTS.** A compound of antimony fluoride with ammonium sulphate used as a mordant (*v.* ANTIMONY).

**ANTIPYRINE.** *Phenyldimethylpyrazolone.* This substance, a valuable febrifuge and analgesic, was discovered by Knorr in 1884, and investigated therapeutically by Fehlen. Phenylhydrazine reacts with aceto-acetic ether according to the following equation

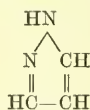


with the formation of the phenylhydrazone of acetoacetic ether.

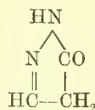
On heating this compound to 100° one molecule of alcohol is liberated and a substance is formed containing a ring of five atoms, two nitrogen and three carbon atoms:



The simplest base of which this body is a derivative is known as *pyrazole*:

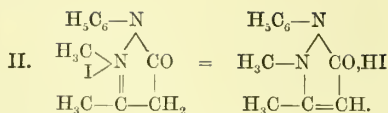
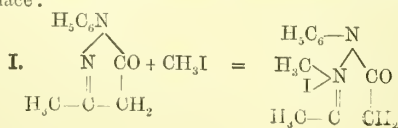


and the body containing one carbonyl group is *pyrazolone*:



hence the derivative above obtained is a phenylmethylpyrazolone. This substance is mixed with equal parts of methyl iodide and methyl alcohol and heated to 100° when phenyldimethylpyrazolone is obtained. The dark mass is decolourised with sulphurous acid, after which the alcohol is distilled off and the antipyrine precipitated as a heavy oil with sodic hydrate. The solution is extracted with ether in which it is not very soluble and finally purified by crystallisation from toluene.

The reaction probably takes place so that the phenylmethylpyrazolone forms an addition product with one molecule of methyl iodide, and afterwards a molecular rearrangement takes place:



Antipyrine melts at 113° and crystallises in small plates. It is a strong monovalent base, but only the picrate and platinum double salt crystallise easily (*v.* PYRAZOLE).

**ANTISEPTICS** *v.* DISINFECTANTS.

**ANTITHERMIN** *Phenylhydrazinelevulinic acid*  $\text{C}_6\text{H}_5\text{C}(\text{N}_2\text{H.C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$  is obtained by dissolving phenylhydrazine in dilute acetic acid, adding an aqueous solution of the equivalent quantity of levulinic (acetopropionic) acid, and crystallising the resulting yellow precipitate from alcohol (Farbw. vorm. Meister, Lucius & Brüning in Höchst a. M., Germ. Pat. 37,727).

It forms colourless, inodorous, and tasteless scales, melts at 98°-99°, is sparingly soluble in cold water, soluble in alcohol, ether, and dilute acids. It has been employed as an antipyretic (Nicot, C. C. 1887, 415); but, according to Stark (Chem. and Drug, 32, 651), its use in medicine is now almost abandoned. Inasmuch as it is decomposed by alkalis, its physiological activity is probably due to phenylhydrazine (Gehe & Co., C. C. 1888, 49).

**ANTIRRHINIC ACID** *v.* DIGITALIS.

**ANTWERP BROWN** *v.* PIGMENTS.

**ANVULA** *v.* AMLAKI.

**AODD-I-BALSAM** *Balsam of Mecca* *v.* OLEO-RESINS.

**APATITE** (*ἀπατώ*, to deceive). A name proposed by Werner, in 1786, for the native crystallised calcium phosphate of Saxony, in consequence of the deceptive appearances which the mineral often presents, and since extended to all minerals of like chemical composition. Apatite crystallises in forms belonging to the hexagonal system, frequently in short, six-sided prisms, each terminated either by a pyramid of as many faces or by a simple flat plane. The horizontal edges at the ends of the crystal are often variously modified, and the lateral faces of the prism frequently exhibit vertical striae. Cleavage is generally not well marked. The mineral varies in colour from white to violet and brown; but the streak is always white. As a rule the lustre is glassy, but inclined to be resinous. Some varieties of apatite are transparent, others are quite opaque. Its specific gravity varies from 2.92 to 3.25; it is harder than glass, but not so hard as felspar. All apatites consist mainly of calcium phosphate associated to a greater or less extent with either calcium chloride or fluoride, or with both. Their general composition may be thus formulated:— $[\text{3}(\text{Ca}_3\text{P}_2\text{O}_8) + \text{Ca}(\text{Cl}_2, \text{F}_2)]$ ; the chlorine, however, may be altogether absent, the mineral then becoming a Fluorapatite or Francolite. The amount of phosphoric anhydride in apatite varies from 40 to 45 p.c. The mineral fuses with difficulty before the blowpipe. Many varieties are phosphorescent when heated, and become electric by heat and friction. Apatite is found in veins at St. Michael's Mount, and in several Cornish tin-mines; as Francolite in crystalline masses at Huel Franco and Fowey Consols, in Cornwall. Important deposits exist at Oedegarten, Bamle, Norway; at Logrossan,

Estremadura, Spain; and at Staffel, near Limburg, on the Lahn and elsewhere in Nassau. In Canada eight varieties of apatite occur in large quantities, containing from 74.29 to 89.68 p.c. of calcic phosphate (Hoffmann, C. J. [2] 40, 525), one bed being five m. thick (Hutton, C. N. 21, 150). In the United States there are also a large number of localities yielding apatite; at Hurdstone, New Jersey, masses weighing 200 lbs. have been mined. The apatites found in the departments of Lot and Tarn-et-Garonne contain iodine. When apatite is treated with sulphuric acid it is converted into superphosphate of lime, and in this soluble form is highly valued as a manure. It is also used as a substitute for bone-ash in the manufacture of certain kinds of soft porcelain.

Ditte has made apatite by fusing calcic phosphate with sodium chloride (C. R. 94, 1,592; J. 35, 10), *v. CALCIUM*.

**APHTHITE.** An alloy containing 800 parts of copper, 25 of platinum, 10 of tungsten, and 170 of gold (Zeits. f. d. C. Grossgew. 4, 313).

**APIGENIN** *v. GLUCOSIDES*.

**APIIN** *v. GLUCOSIDES*.

**APIOS TUBEROSA** or **GLYCINE APIOS**.

A leguminous plant from North America, the roots of which have been proposed as a substitute for the potato, and the young seeds for peas. Payen (C. R. 28, 189) gives the following analysis of the root:—Nitrogenous matters 4.5, fatty matters 0.8, starch, sugar, &c. 33.55, cellulose &c. 1.3, inorganic 2.25, water 57.8.

**APLOTAXIS AURICULATA** *v. COSTUS*.

**APORETIN** *v. RHUBARB*.

**APOTURMERIC ACID** *v. TURMERIC*.

**APPLE.** The fruit of the apple tree. A recent analysis of apples by Bertram (B. C. 7, 59) gave:—Water 32.12, albuminoids 1.06, fibre 5.59, extractive free from nitrogen 58.97, ash 1.96, glucose 39.71, cane sugar 3.90, starch 5.22, free acid 2.68, pectinous substances 4.54, remainder 2.92. Other analyses of apples are given in **WATTS' DICTIONARY** (first edition), vol. ii. 715.

Truelle (Bl. [2] 27, 398; C. J. [2] 32, 514) was unable to find any relation between the proportion of sugar contained in apples and their acidity.

Zinc has been found in dried American apple chips (S. C. I. 5, 498), *v. CIDER*.

**APPLES, ESSENCE OF.** Iso-amyl isovalerate, dissolved in ordinary alcohol. Used in perfumery.

**APPLETREE.** (*Pyrus malus*, L.; *Pomme*, Fr.; *Apfel*, Ger.) The wood is much used in turnery, and that of the crab tree is used by millwrights for the teeth of mortice wheels. The bark contains a tannin identical with that contained in horse-chestnut bark.

**APOMORPHINE** *v. VEGETO-ALKALOIDS*.

**APHYLLITE** *v. CALCIUM*.

**APRICOT OIL.** (*Chooli-ki-tel*; *Badam Kohee*.)

Expressed from the kernels of *Prunus Armeniaca*. It is of a pale yellow colour, smelling of prussic acid; has a bland taste; sp.gr. at 60° = 0.9204; its freezing point is below that of almond oil. With nitric acid it gives a coffee-brown colour; a light brown with sulphuric acid, and, with the elaidin test, a light yellow hard mass, solidification taking place in about two hours.

Used in cooking, as a burning oil, and as a cosmetic (Maben. Ph. [3] 16, 798).

**APRICOT, ESSENCE OF.** A mixture of iso-amyl butyrate and iso-amyl alcohol.

**AQUA FORTIS** *v. NITRIC ACID*.

**AQUA REGIA.** *Nitromuriatic acid*; *Königswasser*. A name given by Basil Valentine to a mixture of nitric and hydrochloric acids, originally prepared by dissolving sal ammoniac in strong nitric acid, and used by the alchemists as a solvent for gold, sulphur, &c. Usually made by mixing 1 vol. of nitric acid with 4 vols. of hydrochloric acid. The mixture is at first colourless, but gradually—especially on heating—acquires a deep orange yellow colour, due to the formation of nitrosyl chloride and free chlorine:  $\text{HNO}_3 + 3\text{HCl} = \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$ . The solvent action of aqua regia appears to be mainly due to the free chlorine.

**AQUA VITE.** A name used by Avicenna to denote common alcohol as obtained by distilling a liquid which has undergone vinous fermentation.

**ARABIC GUM**, *v. GUMS*.

**ARABINOSE**  $\text{C}_5\text{H}_{10}\text{O}_5$ , [(Kiliani, B. 20, 339 and 1233, and 21, 3006); (Griess and Harrow, B. 20, 3111; and Brown and Morris, C. J. 51, 619)]  $\text{C}_6\text{H}_{12}\text{O}_6$  (Scheibler, B. 1, 58 and 108; 6, 612; and 17, 1729). A substance crystallising in well-defined rhombic prisms, obtained by the action of sulphuric acid on beet gum, cherry-tree gum, gum arabic, and allied gums.

*Preparation.*—A solution of gum arabic, or allied gum (dextrorotatory, and yielding little mucic acid by the action of nitric acid, by preference), containing 30 to 40 grams of the gum and 2 to 3 c.c. sulphuric acid in 100 c.c., is boiled for seven to twelve minutes, cooled, the acid neutralised with calcium or barium hydroxide or carbonate and alcohol, sp.gr. .83, added as long as a precipitate is produced. This precipitate soon settles, leaving the alcoholic solution clear. On distilling off the alcohol and evaporating to a syrup, arabinose crystallises out. The substance is obtained in well-defined rhombic prisms with monoclinic termination by recrystallising from water. With some gums the digestion of the acid solution can be continued for two hours with increased yield of arabinose, and without impairing the purity of the product. The crystals are anhydrous; they melt at 160°.

Arabinose is optically active,

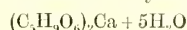
$[\alpha]_D = +104.4 - +105.4^\circ$  (Scheibler);

$[\alpha]_D +104.7^\circ$  to  $+108$  (O'S.),

the activity increasing with the strength of the solution in which it is observed. The activity of freshly-prepared solutions is 1.5 to 1.6 times greater than the permanent activity—*i.e.* the activity in solutions after boiling or long standing in the cold (O'Sullivan, C. J. 45, 51). It exhibits the power of bi-rotation (Griess and Harrow).

It reduces alkaline solutions of the heavy metals; if the amount of copper oxide reduced from Fehling's solution by a given weight of dextrose be taken as 100, the reduction produced by the same weight of arabinose is 110 to 112.

Treated with bromine in excess, arabinose is converted into araboic acid,  $\text{C}_5\text{H}_8\text{O}_6$ , which, on separating from solution, crystallises as a lacton  $\text{C}_5\text{H}_6\text{O}_5$ . The calcium salt crystallises as





(Bauer, J. f. pr. Chem. [2] 34, 47); Kiliani, B. 19, 3030).

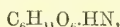
Oxidised with nitric acid, it yields oxalic acid; in the early stages of the reaction, another acid, like saccharic acid, is also present. When 1 part arabinose is digested with 2 parts nitric acid, sp. gr. 1.2, in a water-bath at 35° for six hours, araboic acid is produced. This acid is the same as that obtained by the action of bromine. If 2½ parts nitric acid are employed, and, after digestion at 35°, the solution is evaporated on a water-bath until the evolution of gas ceases, trihydroxyglutaric acid,  $C_5H_8O_7$ , is produced. The potassium salt of this acid is  $C_5H_6O_7K_2$  (Kiliani, B. 21, 3006).

Sodium amalgam (nascent hydrogen) converts arabinose into arbutol (Scheibler, B. 18, 1321), which, according to Kiliani (B. 20, 1233), is normal pentoxypentanol



It would probably be more correct to say that this body is amongst the products of the action of nascent hydrogen on arabinose.

Allowed to stand for some time in a solution containing 60 to 70 p.c. hydrocyanic acid, a crystalline powder falls out which contains  $C_5H_{10}O_7HCN$ ; this, on digestion with hydrochloric acid, yields the amide

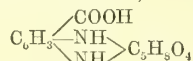


and finally the acid, arabinose carbonic,  $C_5H_{12}O_7$ , which separates from the solution as a crystallisable lacton  $C_5H_{10}O_6$ . This substance, on treatment with hydriodic acid, yields the lacton of hydroxycaproic and normal caproic acid.

Arabinose forms crystallisable compounds with the aromatic diamines and diamido-acids. With *o*-amido-benzol it gives



with  $\gamma$ -diamido-benzoic acid,

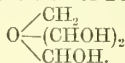


(Griess and Harrow, *loc. cit.*). A solution of 1 part arabinose, 2 parts hydrochlorate of phenylhydrazin, and 3 parts sodium acetate in 20 parts water, when heated for some time on a water-bath, yields a precipitate phenyl-arabinosazone  $C_{11}H_{20}N_4O_3$ ; its fusing point is 157° to 158°.

These facts have led to the conclusion that arabinose is a  $C_5H_{10}O_5$ , and that its constitution is



or, according to the view of Tollens,



Continued heating with dilute acids decomposes it, levulinic acid not being one of the products; other acids are present (Tollens). It is doubtful whether the body is fermentable with ordinary beer yeast. On these latter grounds it is considered not to be a glucose.

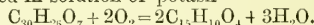
O'S. and H.

ARACHIDIC ACID v. FATTY ACIDS.

**ARALIA BARK** or **FALSE PRICKLY ASH BARK**, the bark of *Aralia spinosa*, contains a volatile oil, an amorphous bitter substance, (tannin), a grey acrid resin, and a glucoside to which the name aralëin has been given (Lilly, Ph. [3] 13, 205). By boiling aralëin with dilute hydrochloric acid, aralëitin is obtained (Holden, Ph. [3] 11, 210; C. J. 40, 105).

**ARAROA POWDER.** *Goa Powder*; *Chrysarobin*. A powder varying in colour from a pale primrose yellow to bronze and purple, which collects, possibly as the result of oxidation of the resin, in the cavities of the stems and branches of the *Andira araroba* (order, *Leguminosæ*) (Aguilar), a tree inhabiting the forests of Bahia in Brazil (Aguilar, Ph. [3] 10, 42; cf. Greenish, *ibid.* [3] 10, 814).

Crude Araroba was analysed by Attfield in 1875 (Ph. [3] 5, 721) and found to contain moisture 1 p.c., glucoside, bitter constituent and arabin 7 p.c., yellow crystalline substance extracted with benzol, supposed to be chrysophanic acid, 80-84 p.c., resins 2 p.c., woody fibre 5.5 p.c. On incineration 0.5 p.c. of ash was obtained. The yellow crystalline compound which constitutes the chief part of Goa powder and to which its activity is probably due, was subsequently examined by Liebermann and Seidler (B. 11, 1603; A. 212, 29). It was shown to be *chrysarobin*  $C_{30}H_{22}O_7$ , independent of, but closely related to chrysophanic acid. It is purified by recrystallisation from glacial acetic acid, m.p. 170-178°; heated with zinc-dust it yields methylanthracene. Chrysarobin is readily converted into chrysophanic acid by the oxidising action of the air. This is most expeditiously effected by leading a current of air through Goa powder dissolved in solution of potash



Liebermann and Seidler describe a *tetraacetyl derivative*  $C_{30}H_{22}Ac_4O_7$ , which melts at 228-230°.

Chrysarobin dissolves in sulphuric acid with a yellow to orange colour, and with strong potash it gives a yellow solution with dark-green fluorescence, becoming red on exposure to air. A minute quantity (1 milligram) of chrysarobin sprinkled on a drop of fuming nitric acid gives a red solution which, when spread in a thin layer and treated with ammonia, strikes a violet colour (Pharm. Germ.).

Though sometimes administered internally as a purgative, araroba powder is used in medicine almost exclusively as an external remedy in the form of ointment, in the treatment of certain skin diseases.

A. S.

**ARASINA GURGI.** An impure gamboge from Camara, obtained probably from a species of *Garcinia* (Dymock, Ph. [3] 7, 451).

**ARBOL-A-BREA RESIN.** Is obtained from *Canarium album*, a tree belonging to the Burseraceæ, growing in the Philippines. The residue is greyish-yellow, soft, glutinous, and has a strong agreeable odour. It contains 61.29 parts of resin very soluble in alcohol; 25.00 parts of resin sparingly soluble in alcohol; 6.25 essential oil; 0.52 free acid; 0.52 bitter extractive matter; 6.42 woody and earthy impurities (Bonastre, J. Ph. 10, 129). Baup has isolated four crystalline substances, Amyrin, Breidin, Brein, and Bryodine (A. Ch. [3] 31, 108).

ARBUTIN v. GLUCOSIDES.

**ARCHIL** or **ORCHIL**. (*Orseille*, Fr.; *Orseille*, Ger.; *Orieello*, It.) Appears in commerce in three forms: (1) as a pasty matter called *archil*; (2) as a mass of a drier character, named *persis*; and (3) as a reddish powder called *eudbear*. It is obtained from various lichens of the genus *Roccella*, growing on the rocky coasts of the Azores, the Canary and Cape de Verd Isles, also of the Cape of Good Hope, Madeira, Corsica, Sardinia, &c., and from *Ochrolechia tartarea*, growing in Sweden and Norway. None of these lichens contains the colouring matters ready formed, but they contain certain colourless acids, *erythric*, *lecanoric acids*, &c., which are susceptible of transformation into a colourless neutral body, oreicin  $C_7H_5O_2$ , and this, when acted upon by the air and ammonia, changes into a purple substance called oreicin,  $C_7H_5NO_3$ , which is the colouring principle of archil. Archil also contains two other colouring matters of unknown composition termed azoerythrin and erythroleic acid. To prepare archil, the lichens are ground up with water to a uniform pulp, stale urine or ammonium carbonate with a little quicklime is added, and the whole is allowed to ferment with frequent stirring to promote the access of air. In about a week a violet colour is developed, which in a few days becomes brighter and then constitutes ordinary archil. If sodium or potassium carbonate be added to the lichens as well as ammonia, a different change takes place, and a blue colouring matter known as *litmus* is obtained.

Archil, although a fugitive dye, is a very useful ingredient in dyeing, as it gives a brilliant lustre to the goods. The colour is made more permanent by using a solution of tin with it, but the archil loses its natural colour and assumes one approaching more or less to scarlet, according to the quantity of solution of tin employed.

Prepared archil very readily parts with its colour to water and to alcohol; it is the substance principally made use of for colouring the spirit in thermometers. As exposure to the air destroys its colour upon cloth, so does the exclusion of the air produce a like effect in these hermetically sealed tubes. Abbé Nollet in 1742 observed that the colourless spirit, upon breaking the tube, soon resumes its colour, and this for a number of times successively.

Archil, applied to marble, stains it a beautiful violet or purplish-blue colour which is far more durable than the colour it communicates to other bodies.

Oreicin has been made by Nevile (E. P. 4,389, 1881; B. 15, 2976; S. C. I. 1, 228, 2, 167) from metadinitrotoluene; by Vogt a. Henninger in 1872 from  $\alpha$ -chlorotoluenesulphonic acid; and by Cornelius a. Pechmann (B. 19, 1446; S. C. I. 5, 481) from acetone dicarboxylic acid.

Archil is often adulterated with coal-tar colours and with extracts of logwood, redwood, &c. Several methods for the detection of such adulterations have been proposed. Thus, to detect magenta, Kertess (D. P. J. 256, 281) tests by boiling with a large excess of water and filtering, and adding benzaldehyde, a tin salt, and hydrochloric acid to the filtrate, which is then well shaken and allowed to stand, when, if magenta

is present, the lower layers assume a red colour. Fairley (S. C. I. 5, 286) tests for magenta by extracting the paste with strong aqueous ammonia until all the natural colour is removed, when, on adding alcohol to the residue, the aniline dye appears of its proper colour.

Azo- colours are also not unfrequently added to archil. The modes of detecting these and other colouring matters which may be added have been examined by F. Breint (Mitth. d. Techn. Gewerbemuseums in Wien; S. C. I. 1888, 345). An adulteration of archil colouring matters with logwood or Brazil wood may be shown by a dye trial with mordanted cotton. Cotton yarn or cloth mordanted with iron or alumina salts answers the purpose best. The cotton stuff is dyed for half an hour in the hot solution of the suspected sample, which before has been boiled and suitably diluted; it is then washed in a warm solution of soap. Pure archil or eudbear produces scarcely any colour on mordanted cotton (an extremely faint pink only), whilst a sample containing an extract of logwood or redwood dyes the cotton readily, extract of logwood dyeing cotton mordanted with iron salts bluish-grey or black, if mordanted with alumina salts, bluish-violet. By the redwood, cotton mordanted with iron salts is dyed a blackish-brown, if mordanted with alumina salts, red. (Comp. Crossley, J. Soc. Dyers and Colourists, 1885, 23; Knecht, *ibid.* 1887, 23; Liebmann and Stude S. C. I. 1886, 287; Rawson, Journ. Soc. Dyers and Colourists, 1888, 68.)

Archil is also used to impart to white wines the colour of sparkling wines, but its presence can be detected by precipitating with lead acetate and extracting with amyl alcohol, when a red colour indicates the presence of archil or magenta. The addition of a little hydrochloric acid changes the colour to yellow if magenta be present, but does not alter it if archil has been employed (Hass. Fr. 20, 369; S. C. I. 1, 119).

By heating two molecules of oreicin and one molecule of benzoic acid with sulphuric acid at  $130^{\circ}$ - $135^{\circ}$  for four hours, Zulkowsky (M. 5, 221; S. C. I. 3, 441) obtained a substance giving in alcoholic solution a beautiful gold-yellow colour.

Rousse! (C. C. 19, 368; S. C. I. 3, 516) uses *roccellin*, prepared by diazotising naphthylamine sulphonic acid and combining it with  $\beta$ -naphthol, as a substitute for archil, but it has not yet been fixed upon vegetable fibre (v. AZO-COLOURING MATTERS).

Oreiu may be quickly estimated in a sample by adding a known quantity of bromine in excess, with which it combines forming insoluble tribromorein, and then determining the excess of bromine (Reyman, Z. 8, 790; C. J. [2] 13, 1293).

**ARCHIL BROWN** v. AZO-COLOURING MATTERS.

**ARCHIL RED** v. AZO-COLOURING MATTERS.

**ARCHIL SUBSTITUTE** v. AZO-COLOURING MATTERS.

**ARECA**. A genus of palms containing the important species *Areca catechu* (*betel nut* or *arcca nut*), the fruit of which is used as a masticatory in the East Indies. It contains an inferior catechu, tannic and gallic acids, ammonium acetate, fats, oils, gum, nitrogenous

substances, and a dye (*areca red*). The charcoal of the nut is used as a tooth powder, and the ground nut is employed as a remedy for tape-worm. According to Ure one tree will produce from 200 to 800 nuts according to its age, situation and culture. The tax on the areca nut produce in India during the year 1835-6 was 335,000 rupees (Chem. and Drug. 29, 850).

**AREOMETER** *v.* **HYDROMETER**.

**ARGAL** *v.* **ARGOL**.

**ARGAL OIL**. An oil obtained from the kernels of *Argania Sideroxyylon* (order, *Sapotaceæ*), growing in Morocco. The kernels are first roasted, ground to powder and mixed with water, when the oil separates (Ph. [3] 10, 127).

**ARGENTAN**. *Aluminium bronze*, *v.* **ALUMINIUM**.

**ARGENTINE**. Finely divided spongy tin, made by reducing a weak solution of tin salt (120 grammes in 60 litres of water) by zinc. The tin is collected in a sieve, washed with water, and dried at a gentle heat. Used for tin plating and also for printing upon fabrics and paper (Deut. Ind. Zeit. 23, 255; S. C. I. 1, 504).

**ARGOL** *or* **ARGAL**. (*Tartre brut*, Fr.; *Weinstein*, Ger.) Crude bitartrate of potash, known as red argol (*Cremore di Vinaccia*), or white argol (*Cremore di St. Artimo*), according to whether it is deposited from the red or the white grape. The value of the argol made in South Italy is estimated by Kaemmer (C. Z. 9, 949, 1012; S. C. I. 4, 494) at 15,000,000 marks (*v.* **TARTARIC ACID**).

**ARGYRODITE** *v.* **GERMANIUM**.

**ARGYRO-PYRITES**. A silver ore containing 29.75 p.c. Ag; 36.28 Fe; 32.81 S.; sp.gr. = 4.06-4.12. Streak deep-black (Weisbach, J. M. 1877, 906; C. J. [2] 34, 381).

**ARIBINE** *v.* **VEGETO-ALKALOIDS**.

**ARICINE** *v.* **VEGETO-ALKALOIDS**.

**ARMENIAN BOLE** *v.* **PIGMENTS**.

**ARNATTO** *v.* **ANNATTO**.

**ARNOTTO** *v.* **ANNATTO**.

**ARNICA** *v.* **RESINS**.

**AROMATIC VINEGAR** *v.* **ACETIC ACID**.

**AROXENE** *v.* **VANADIUM**.

**ARRACK**. (*Arack*, Fr.; *Arak*, Ger.) A spirituous liquor imported from the East Indies. The finer qualities are distilled from the fermented juice (toddy, palm wine) of the cocoanut; the other kinds from rice or sugar fermented with cocoanut juice, and they are made more intoxicating by the addition of poppy-heads, hemp leaves, juice of stramonium, &c. (Cooley, 1).

**ARRAGONITE** *v.* **CALCIUM**.

**ARROPE**. Sherry boiled to a syrup, used for colouring other wines.

**ARROWROOT**. (*Racine fléchère*, Fr.; *Pfeilwurzeln*, Ger.)

This term is applied generically to indicate a starch or fecula; thus Portland arrowroot is obtained from *Arum maculatum*; East India arrowroot, from *Curcuma angustifolia*; Brazilian, from *Manihot utilisima*; Tahiti arrowroot, from *Tacca pinnatifida*; English arrowroot, from the potato.

True arrowroot, however, is the starch of the *Maranta arundinacea*, now cultivated in the East and West Indies, Natal, and Australia.

In Ure's Dictionary, a full description of the process of preparing arrowroot on the Hopewell estate, St. Vincent, West Indies, is given, and in the J. S. A. 30, 1013, and Pharm. J. Trans. [3] 13, 224, the details of its manufacture in Queensland are described; the essential part of the process being that the roots are reduced to a pulp with water, the fibrous matter separated, and the starch allowed to settle in large tanks.

A plot of ground 22½ × 32 feet planted with *Maranta arundinacea* in the Shevaroy Hills, India, produced 430 lbs. of corms yielding 65 lbs. of arrowroot.

Drawings of the microscopic structure of arrowroot are to be found in Allen's Organic Analysis 1, 339, and Ph. [3] 6, 204.

Cavassa starch has been found as an adulterant.

An analysis of arrowroot biscuits by Stutzer (Russ. Zeitschr. Pharm. 21, 724; J. 21, 724) gave albuminoids 6.71, fats 12.21, carbohydrates 73.67, water 6.53, ash 0.88, phosphoric acid 0.236.

**ARSENARGENTITE**. An ore containing 81.37 p.c. of silver and 18.43 of arsenic (Hannay, Min. Mag. 1877, 849; C. J. [2] 34, 15).

**ARSENIC**. (*Arsenic*, Fr.; *Arsenic*, *Arsen*, Ger.) *Schwerbennkobalt*, *Fliegengift*, *Näpfchenkobalt*. *Arsenicum*. *Regulus Arsenici*.

Symbol, As; at wt. 74.9 (Berzelius, Pelouze, Kessler, Dumas).

*Occurrence*.—Arsenic, in small quantities, is one of the most widely distributed elements; it is found in mineral and other waters, and in coal smoke, in most pyritic minerals, and in a large number of ores.

In England it occurs principally with *tin ore*, and on the Continent in *mispickel*. Arsenic occurs native (usually associated with iron, cobalt, nickel, antimony, and silver), in crystalline rocks and in the older schists, generally in reniform and stalactitic masses, often mammillated; it also occurs occasionally in rhombohedral crystals. At Zimeoff in Siberia, large masses are found; it occurs in the silver mines of Freiberg, Annaberg, Marienberg, and Schneeberg in Saxony; at Joachimsthal in Bohemia, Andreasberg in the Hartz, Kapnik in Transylvania, Orawitz in the Banat, Kongsberg in Norway, St. Marie-aux-Mines in Alsace, in Borneo, and in the United States.

As *arsenide* it occurs combined with iron in two forms  $FeAs_3$  and  $Fe_2As_3$ ; with nickel as *Kupfernickel*  $NiAs_3$  and  $NiAs_2$ ; with cobalt as *tin white cobalt*,  $CoAs_3$ . With antimony it occurs as *arsenical antimony* at Příbram in Bohemia; with blende antimony and spathic iron at Allemont, at Schladming in Styria and Andreasberg in the Hartz.

Arsenic is generally present in native sulphur. Combined with sulphur it occurs as *realgar* or *ruby sulphur*  $As_2S_2$  in Hungary, Saxony, Switzerland and China; and as *orpiment*  $As_2S_3$  in Hungary and the Hartz.

With sulphur and iron it occurs as *mispickel*, *arsenical pyrites*, or *white mundic*  $FeS_2.FeAs_3$ ; with sulphur and cobalt in *cobalt glance*  $CoS_2.CoAs_3$ ; in *nickel glance*  $NiS_2.NiAs_3$ , and in a number of other ores, being obtained as a secondary product in the roasting of *tin* and *copper*



ores, copper nickel, arsenical fahl ores, smaltine, cobalt and nickel glance, &c.

With oxygen, arsenic occurs as *arsenolite* or *arsenite*  $As_2O_3$ , usually as a crust on other arsenical minerals, being formed by their decomposition. With oxygen and cobalt, it forms *cobalt bloom* or *arsenate of cobalt*; it also occurs as arsenates of iron, copper, and lead.

*Preparation.*—Metallic arsenic is used only to a small extent in commerce. It is usually prepared from native arsenic, arsenical iron or mispickel, the latter being the only mineral used to any extent in England. The mineral used is heated in earthenware retorts or tubes laid horizontally in a long furnace. Great care is required in manufacturing the retorts; a mixture of 1 part fresh clay and 2 parts bricks or old retorts powdered, is made into the proper form, coated with a mixture of blood, loam, forge-scales and alum to produce the glaze, and burned. They are very strong and heat-resisting, and quite impervious to the vapour of arsenic. A piece of thin iron sheet is rolled and inserted into the mouth of the retort and an earthen receiver luted on. On distilling, most of the arsenic condenses in the iron as a nearly white, coherent, internally crystalline mass, and is detached on cooling by unrolling the iron. If required, the arsenic is purified by redistillation.

At Altenberg in Silesia, arsenious oxide is heated with charcoal in an earthen crucible covered with an inverted crucible or conical iron cap. This method is more economical and productive than the one above described, but the metal is grey and pulverulent, and always contains arsenious acid.

It may also be prepared by heating the sulphides with charcoal and sodium carbonate or potassium cyanide.

*Properties.*—Arsenic is a very brittle steel grey metalline mass of sp.gr. 5.62 to 5.96, of brilliant lustre, crystallising in rhombohedra, isomorphous with metallic antimony. It is a good conductor of electricity, and is odourless and tasteless.

It is volatile at temperatures above  $100^\circ$ , and is rapidly vaporised at a dull red heat. At the ordinary pressure it volatilises without previous fusion, the vapour being yellow and of a garlic smell, but when heated under pressure it melts at  $500^\circ\text{C}$ . (Landolt). Joubert states that above  $200^\circ\text{C}$ . its vapour is phosphorescent (C. R. 78, 1855).

When the vapour is condensed at a temperature but little below the volatilising point, *i.e.* when condensed in an atmosphere of arsenic, a nearly white compact mass of strongly metallic lustre is produced which scarcely oxidises in the air even when heated to  $80^\circ\text{C}$ . When it is deposited on a colder surface or in an atmosphere other than arsenic, it forms less dense, dark-grey crystals which readily oxidise in the air even in the cold, and especially on heating.

Ludwig (Ar. Ph. [2] 97, 23) has obtained arsenic (?) with a perfectly bright surface resembling freshly granulated zinc, and of the low density 5.395, by distilling in a tube with a small quantity of iodine.

When heated in air it absorbs oxygen, burning with a bluish flame and forming arsenious

oxide. In pure water it is unaltered, but when exposed to air it forms a grey powder supposed by some to be a suboxide, but probably a mixture of metallic arsenic and arsenious oxide; this powder is sold as 'fly-powder.' When powdered and thrown into chlorine it ignites, forming the trichloride; with the aid of heat it combines with bromine, iodine, and sulphur. Hydrochloric acid has but little action on arsenic, but it is rapidly dissolved by nitric acid, aqua regia or by a mixture of hydrochloric acid and potassium chlorate.

When deflagrated with nitre it forms potassium arsenate.

Bettendorf (A. 144, 110) has obtained a specular, amorphous, vitreous arsenic of sp.gr. 4.69–4.716 by subliming arsenic in a stream of hydrogen and condensing it at  $210^\circ$ – $220^\circ\text{C}$ . At  $360^\circ\text{C}$ . it is converted into the crystalline form with the evolution of considerable heat, and when heated suddenly it hisses and gives off vapour whilst transforming.

Arsenic is a constituent of many alloys; it is used for bronzing brass and for the manufacture of opal glass, and it is burned in oxygen gas as a signal light for trigonometrical surveys.

(For the distribution of arsenic in commercial products *v. Arsenious oxide*.)

*Detection.*—Arsenical compounds, when heated on charcoal, give off the characteristic garlic odour and white fumes of the oxide, with a white incrustation on the charcoal some distance from the assay. Metallic arsenic, and many arsenical minerals, such as mispickel, when heated in a tube closed at one end form a blackish, shining metallic ring on the cooler portion of the tube; if heated in a tube open at both ends the arsenic is oxidised and condenses in a ring of white octahedral crystals, their shape being plainly visible under a lens. On cutting off the closed end of the tube containing the metallic mirror and heating, it is also converted into the white ring higher up the tube. The white crystals dissolve in boiling water, and the solution shows the usual tests for arsenic. Antimony under like circumstances would produce a white ring, which, however, is not crystalline, and is not soluble in water. Oxides of arsenic require to be mixed with charcoal before they produce the black mirror. Sulphides require the addition of alkaline carbonate or potassium cyanide, or they may be heated with baryta alone (Brancé).

White arsenic when heated with about 3 parts of sodium acetate, gives the offensive odour of kakodyl.

In solution the reactions of the two series of compounds, the arsenious and the arsenic, differ considerably; generally speaking, arsenic compounds may be converted into the arsenious form by heating with sulphurous acid or with a sulphite.

*Reinsch's test.* If a piece of clean metallic copper is immersed in a solution of arsenious acid or an arsenious compound acidulated with pure hydrochloric acid, it is coated with a grey film, which is probably an arsenide of copper. The action proceeds better at the boiling temperature. The acid must be first tested in the same manner to insure the absence of arsenic, which is always present in the commercial acid.

The metal is washed, dried gently and heated in a tube, when the arsenic becomes oxidised and forms a *crystalline ring* on the colder part of the tube. A film due to antimony, as mentioned before, would not produce a crystalline ring.

This method is used in testing for and removing arsenic from hydrochloric acid, and in toxicology; by it 1 part of arsenic can be detected in 250,000 parts of solution.

When hydrogen is generated in a liquid containing an arsenious compound, the arsenic combines with it and passes off as the gaseous hydride; many very delicate tests are based on this reaction.

(1) *Fleitmunn's test.* The solution is mixed with excess of caustic potash, a piece of pure zinc, or of magnesium, or aluminium foil inserted, and the solution heated. A piece of filter paper moistened with silver nitrate is held over the mouth of the tube. In presence of arsenic, arseniuretted hydrogen is produced and reduces the silver on the paper forming a greyish or purplish colour. Antimony is not evolved in this test. Fleitmunn's test is therefore a ready means of finding arsenic in presence of antimony; it is not, however, so delicate as Reinsch's or Marsh's method.

(2) *Marsh's test.* This or Reinsch's test is usually used in toxicology. The solution is acidulated with pure hydrochloric acid and introduced into an apparatus in which hydrogen is generated by means of pure sulphuric acid and zinc. Arsenic hydride is formed and is passed through a narrow glass tube, which is heated at one spot by a lamp; the arseniuretted hydrogen as it passes over the heated portion is decomposed with the precipitation of arsenic as a black ring. In testing for very small quantities of arsenic, the action should be continued for about an hour. A blank experiment should always be performed in the same manner to insure the purity of the zinc and acid. On the presence of arsenic in glass as a source of error in the detection of arsenic, *v. W. Fresenius*, *Fr.* 22, 397; *B.* 17, 2938. Instead of heating the tube the gas may be ignited at the mouth of the tube, and the flame caused to impinge on a cold surface of porcelain, or preferably of platinum foil. The arsenic film may be distinguished from that produced by antimony as follows:—(1) The arsenic film is quickly evaporated, while that of antimony only slowly disappears. Helling (*Das Microscop in der Toxicologie*) recommends that small spots be heated and the vapour received on a slip of glass, when, under the microscope, the octahedral crystals due to arsenic are visible.

(2) The arsenic film quickly dissolves in a solution of sodium hypochlorite; the antimony film is very slowly soluble.

(3) The antimony film dissolves quickly in yellow ammonium sulphide, leaving an orange-yellow residue on evaporation; the arsenic film dissolves very slowly.

Magnesium may also be employed in place of zinc, and E. Davy and A. Jandrousch use an amalgam of 1 part sodium in 8 parts mercury, with or without acid.

The presence of nitrates or nitric acid inter-

feres with this test, and the acids used should be dilute.

Bloxam (*C. J.* 13, 14) describes an electrolytic method which is very delicate;  $\frac{1}{10.0}$  grain of arsenic may be detected in a large volume of liquid. It has not been largely used, but it possesses advantages over other methods. (1) only one substance is used which might contain arsenic; (2) the other bodies in solution remain behind either precipitated on the platinum pole or in solution, without admixture with interfering substances, and may be examined; (3) the film produced contains no antimony.

The bottom is cut from a two-ounce narrow-mouthed bottle and replaced by vegetable parchment, tightly stretched with a piece of platinum wire (any organic ligature would soon be destroyed). Through the cork is passed a funnel tube, a delivery tube connected by indiarubber tubing to the reduction tube, and a platinum wire terminating in a negative pole of platinum. The bottle is placed in a glass vessel of slightly greater diameter and an ounce of pure sulphuric acid (1 part acid to 4 parts water) poured into the outer and inner vessels, so that the level shall be equal in each. The positive platinum pole is placed in the outer vessel. A current from six Grove's cells is passed through the solutions, and when the vessel is filled with hydrogen the reduction tube is heated for about 30 minutes while the gas passes through. If no ring appears the acid is free from arsenic, and the solution to be tested is passed through the funnel tube followed by a drachm of alcohol to prevent frothing. The action should be continued for 30 minutes before the absence of arsenic is considered proved.

The addition of a little sulphuretted hydrogen solution to the mixture prevents the possibility of antimony being present in the mirror. When the liquid to be examined is mixed with a large quantity of organic matter, as is frequently the case, it should be boiled with dilute hydrochloric acid (1 to 6) till the organic matter is disintegrated, when the liquid is strained through muslin. Or potassium chlorate may be added in small portions until the organic matter is oxidised. Great care must be used in ascertaining that the acid and even the potassium chlorate are free from arsenic. The organic matter may also be separated by Graham's diffusion method.

If ammonia is added to a solution of copper sulphate till a slight precipitate remains, the mixture produces a green precipitate of Scheele's green with an arsenious compound. Silver nitrate treated with ammonia in the same manner gives a canary-yellow precipitate with arsenious compounds.

*Estimation.*—Arsenic is usually estimated as (1) magnesium pyro-arsenate, or (2) as arsenic sulphide.

(1) For this method it is necessary that the substance should be present as an *arsenic* compound. The conversion from the arsenious to the arsenic condition may be effected by heating with nitric acid (*v.* estimation as sulphide) or with hydrochloric acid and potassium chlorate.

The acid solution, which should occupy only a small bulk, is mixed with a magnesia mix-

ture' and rendered *strongly* alkaline with ammonia. After standing for 24 hours the solution is filtered, the last portions of the precipitate, which consists of ammonium magnesium arsenate, being washed entirely on to the filter paper with a little of the filtrate (the volume of this filtrate should be noted roughly). The precipitate is then washed with a mixture of 1 part strong ammonia and 3 parts water, until only a slight opalescence is produced on the addition of nitric acid and silver nitrate to a few drops of the washings. It is then dried, detached as much as possible from the filter paper, and transferred to a weighed porcelain crucible, moistened with nitric acid, dried and ignited, at first gently, and finally to bright redness. The paper is moistened with nitric acid, dried and ignited on the lid, and the crucible and its contents weighed. The ignited residue consists of magnesium pyro-arsenate  $Mg_2As_2O_7$ , and contains 48.29 p.c. of arsenic.

On account of the solubility of the ammonium magnesium arsenate, an addition should be made to the weight obtained of 0.001 gram for each 16 c.c. of filtrate obtained, not counting the washings.

(2) The arsenic for this method should be in the arsenious form. If *arsenic* compounds are present, they are preferably reduced by passing a current of sulphurous acid through the liquid, the excess of that gas being driven off by subsequent heating. Sulphuretted hydrogen is then passed through the liquid until thoroughly saturated, the liquid left to stand for some time, the excess of sulphuretted hydrogen driven off by heating, and the precipitated arsenious sulphide containing sulphur filtered off. The sulphide is dissolved in ammonia, filtered if necessary, and the arsenic estimated in the solution by one of the three following methods:—

(a) The solution is evaporated to dryness in a porcelain dish, then covered with an inverted funnel, and fuming nitric acid added. After the first violent action has ceased, the liquid is heated on a water-bath until the whole of the sulphur has disappeared and only a small bulk of liquid remains; 'magnesia mixture' is then added, followed by excess of ammonia, and the process followed as already described.

(b) The ammoniacal solution is evaporated to dryness in a porcelain dish, and heated on a sand-bath to drive off the whole of the free sulphur and carbonise any organic matter (which is frequently present in toxicological analysis) without volatilising any of the arsenious sulphide. The residue is again dissolved in ammonia, filtered if necessary, evaporated to dryness and gently heated in a weighed porcelain dish, and weighed as arsenious sulphide  $As_2S_3$  (Mohr, Chem. Toxicologie, 56).

(c) The arsenic in the solution may be estimated by means of standard iodine solution (Champion and Pellet, Bl. [2], 26, 541).

*Separation from other metals.*—Certain heavy metals, if present, would be precipitated with the arsenious sulphide by means of sulphuretted hydrogen. From the sulphides of lead, bismuth, &c., the arsenious sulphide can be dissolved by digestion in ammonium sulphide. The solution would also contain antimony and tin, if present. The separation of

arsenic from these two metals may be performed as follows:—

*From antimony.* The mixed sulphides are oxidised with *aqua regia*, as already described, and tartaric acid solution added, followed by excess of ammonium chloride and ammonia. The latter should produce no opalescence. If a precipitate is produced a further quantity of tartaric acid or ammonium chloride must be added. The solution is then precipitated by 'magnesia mixture,' and the estimation made as before described.

*From tin.* A solution of oxalic acid is added to the solution in the proportion of 20 grams of oxalic acid for each gram of tin supposed to be present. The solution should be sufficiently strong for the acid to crystallise out on cooling. The liquid is heated to boiling and sulphuretted hydrogen passed through for 20 minutes. The liquid is allowed to stand for about 30 minutes, and the arsenious sulphide filtered off. It is quite free from tin.

For the estimation of arsenic in ores, Parnell recommends the following method:—A weighed quantity of the *finely powdered* ore is heated to about 200°C. in a slow current of chlorine gas, the volatilised arsenious chloride being absorbed in a solution of chlorine water. After evaporation of the excess of chlorine, the arsenic may be estimated by any ordinary method. Antimony, if present in the ore, would also volatilise with the arsenic.

#### Alloys of arsenic.

Arsenic combines with most metals, in many cases in atomic proportions, the alloys being then known as arsenides. Many natural arsenides occur as minerals.

The alloys may be prepared (1) by fusing the metals under a layer of borax, or in an atmosphere of some inert gas; (2) by reducing the arsenite or arsenate of the metal with potassium cyanide; and (3) in some cases—as with gold, silver, and copper—by placing arsenic in a solution of a metallic salt. W. Spring (B. 16, 324), has obtained crystalline alloys of arsenic with other metals by repeatedly compressing a mixture of the constituents at 6,500 atmospheres.

When heated out of contact with air, arsenical alloys usually lose a portion of their arsenic; heated in air the arsenic is oxidised, a portion volatilising, and the remainder forming an arsenite or arsenate of the metal. When heated with nitre, arsenates are produced. (For a list of alloys of arsenic in atomic proportions, probably existing as arsenides, v. A. Deschamps, C. R. 686, 1022 and 1065.) Some ancient copper spear heads from Cyprus contained 1.348 p.c. arsenic, and a bronze figure of the Ptolemaic period from Egypt contained 1.479 p.c.

The presence of arsenic generally renders an alloy more brittle, more fusible, and brighter. In Pattinson's process it tends to render the crystals smaller and thus lengthens the time required for draining. Its alloys with iron, zinc, and tin are brittle; with gold and silver, brittle, grey; and with lead and antimony, hard, brittle, and very fusible. The addition of from 3 to 6 parts arsenic to 1,000 lead (with occasionally a



little copper) causes the small shot in falling down the tower to form spheres, instead of elongating, as they have otherwise a tendency to do. The arsenic is frequently added in the proper proportions in the form of an alloy of lead and arsenic known as 'temper;' this is prepared by fusing together arsenious oxide and lead. By heating a mixture of lead and arsenic to whiteness, Berthier obtained an alloy of the formula  $Pb_3As$ , any excess of arsenic beyond that corresponding to this formula being volatilised at that temperature. With copper it forms white, malleable, dense, and fusible alloys. White copper contains about 10 p.c. arsenic. Arsenic is also used in speculum metal

and is frequently present in common Britannia metal.

With potassium and sodium arsenic forms alloys which evolve arseniuretted hydrogen when placed in water. With platinum it forms a fusible alloy, and was formerly used to facilitate the working of that metal.

**Arsenic trihydride.** *Arsenietted or arseniuretted hydrogen.* *Arsine.*  $AsH_3$ . This gas is formed whenever hydrogen is liberated in a solution containing arsenious acid or an arsenite, as when zinc is introduced into an acid solution of the substance. It is a colourless, neutral, disagreeably smelling gas, slightly soluble in water, and highly poisonous, even when much

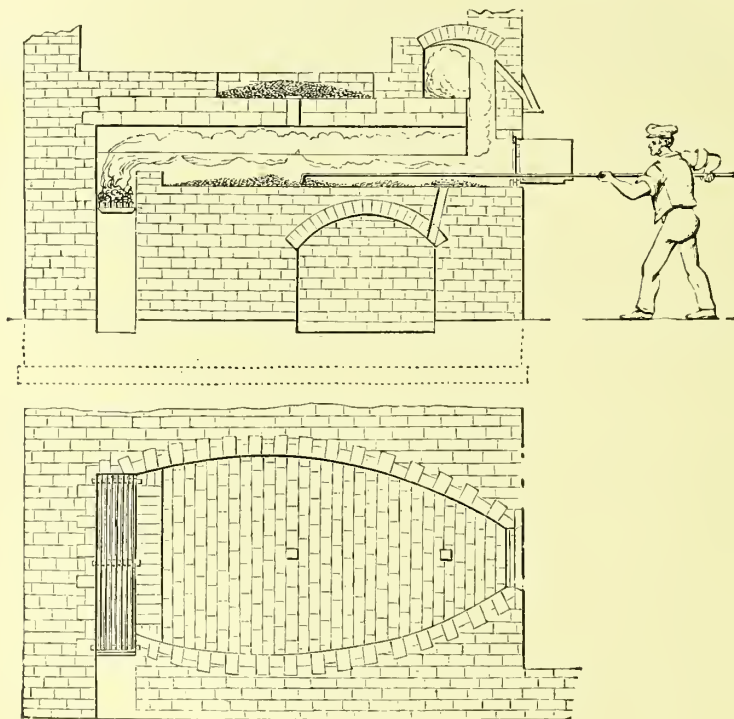


FIG. 1.

diluted. At a red heat it decomposes into arsenic and hydrogen.

It is evolved in the bronzing of brass with arsenic, in tinning sheet iron and frequently in the desilverisation of lead with zinc and subsequent heating of the argentiferous zinc with acid. It is also occasionally present in the air of rooms of which the wall-paper is coloured with arsenical pigments (*v. Schveinfurth green*). It is a very powerful reducing agent, precipitating silver, gold, and other metals from their solutions. Methods for the quantitative estimation of arsenic are based on this property.

A solid hydride of arsenic appears to exist.

**Arsenious oxide.** *Arsenious acid.* White arsenic. *Flowers of arsenic*; commonly known as 'arsenic.'  $As_2O_3$ .

**Preparation.**—In Cornwall, Devon, and at Swansea, arsenious oxide is principally prepared by roasting mispickel, which occurs mixed with iron and copper pyrites, tin ore, wolfram, blende, galena, &c. These ores, if present in sufficient quantity, are separated as far as possible before roasting; tinstone by washing the finely powdered ore, and the other minerals by hand. Arsenious oxide is also largely prepared by roasting arsenical silver at Andreasberg, and from arsenical ores of nickel and cobalt.

In ores from which arsenic is produced as a principal product, the arsenical pyrites generally occurs to the amount of about 12 p.c.

The ores are usually roasted in a reverberatory furnace. In a common form, the furnace bed is flat, 12 to 15 ft. long and 7 to 9 ft. wide

in the middle; the arch is about 2 ft. above the bed, and sinks gradually towards the flue, at which end there is an iron door, through which the ore is raked (fig. 1).

From 8 to 15 cwt. of the stamped dried ore is introduced through a hopper over the centre of the firebridge and spread over the furnace bed. The heat is raised to dull redness and the ore is frequently stirred to ensure thorough oxi-

dation of the arsenic and sulphur. In about 10 hours these have been expelled as oxides, and the arsenious oxide together with some of the sulphur collects in the flues. The spent ore is removed through an aperture in the bed which is closed with an iron door during calcination.

Two such furnaces are sometimes built side by side, separated by a wall, and with their flues

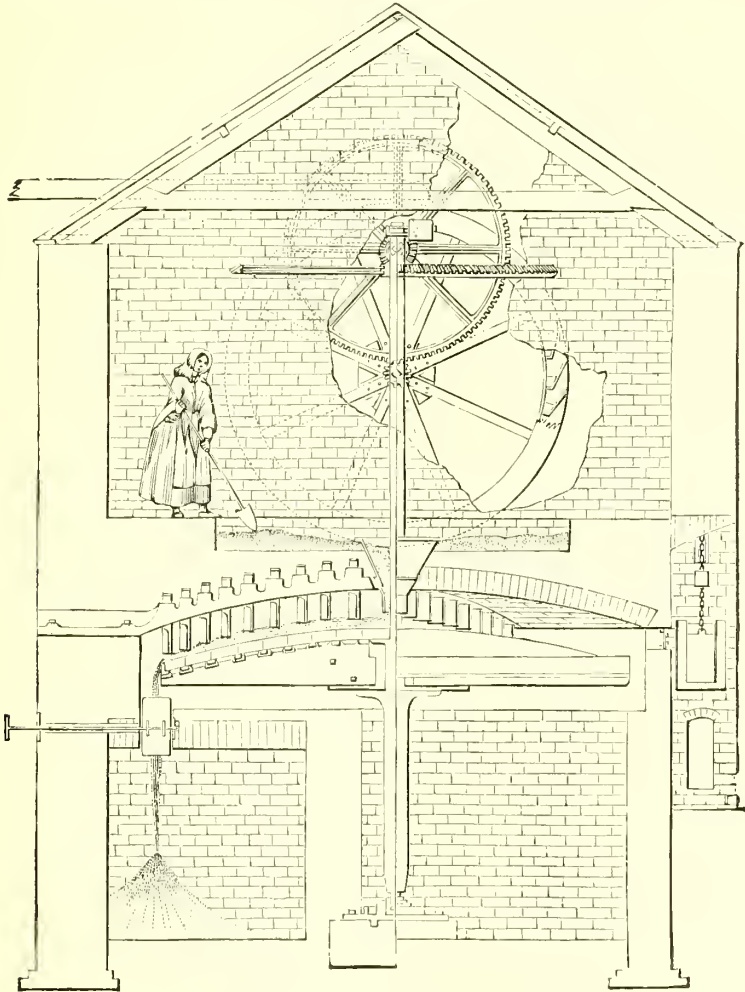


FIG. 2.

uniting. The furnace beds slope gently towards a narrow fireplace. In the first instance the ore is introduced through a number of doors on each side of the furnace. As the ore is worked downwards its place is constantly supplied by fresh ore through an opening in the roof.

*Branton's Calciner* is much used in Cornwall. It is practically a reverberatory furnace with a revolving bed. The bed is of fire-brick resting on a cast-iron table, and is higher at the centre than at the periphery. It is

usually 8 or 10 ft. in diameter; it revolves three or four times in an hour by steam or water power, about half horse power being required. There are two furnaces on opposite sides of the bed (fig. 2).

The dried and finely stamped ore is introduced through a hopper over the centre of the bed. Above the bed are fixed radially three cast-iron frames in which are fastened a number of equidistant iron scrapers shaped like the coulter of a plough and placed obliquely, so that, as the

bed revolves they turn the ore over and outwards towards the periphery of the bed. It is thus

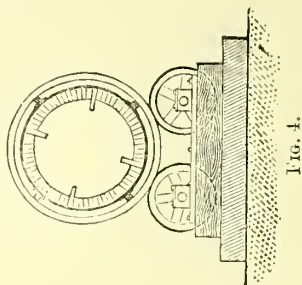


FIG. 4.

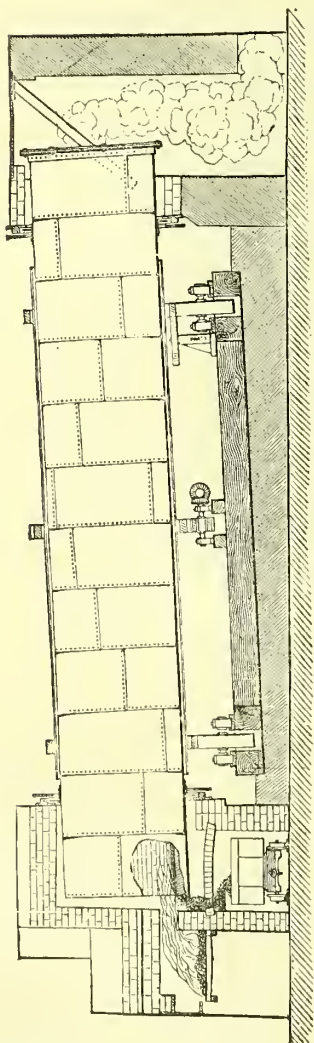


FIG. 3.

thoroughly roasted and, on reaching the edge, falls into a chamber beneath.

*Oxland and Hocking's Patent Calciner* (English Pat. 1868, 2,950) is largely used, especially for 'rank' ores (figs. 3 and 4). It consists of a wrought-iron cylinder, which, if 32 ft. in length, is lined with sufficient firebrick to leave 4 ft. clear internal diameter. Four longitudinal ribs of firebrick occur within the furnace, leaving sufficient space at the upper end for the continuous supply of the ore. The cylinder is generally mounted in an inclined position, usually the slope being  $\frac{1}{2}$  to 1 inch per foot, and is turned by means of a turbine or water-wheel once in 8 or 10 minutes upon friction-wheels.

The dried, finely powdered ore is introduced through an archimedean screw, or from a hopper at the upper end, and in the revolution of the tube becomes lifted to a certain height by the ribs of firebrick, and falls in a fine stream through the hot blast. In a few revolutions the ore is completely oxidised, the arsenic burning off first, and finally reaches the lower end of the tube where it falls through a chamber beneath. A calciner of the above size will roast 6 or 7 tons of ore in 24 hours. In this furnace the amount of air required is minimised, thus rendering the condensation less difficult. The amount of fuel used is also small (*v. further*, Henderson, Proc. Roy. Inst. Mech. Engineers, 1873).

A modification of this furnace has recently been patented by R. and C. Oxland (Eng. Pat. 1885, No. 7,285). It is so arranged that the products shall pass into the condensing chambers unmixed with other gases. At the lower end of the rotating tube is a cast-iron prolongation, heated externally by a grate and a system of flues surrounding it. At the end of the prolongation is a door for removing the calcined products and a regulator for admitting the required amount of air.

At the Devon Great Consols, both Brunton's calciner and Oxland and Hocking's calciner are used.

*Roasting in muffle furnaces.*—This process is used at Altenberg (figs. 5, 6, and 7) and at Reichenstein in Silesia (figs. 8 and 9), where wood is cheap.

The ore, reduced to a moderate size and known as *schleich*, is introduced through an opening in the top in charges of about 10 cwt. and spread 2 or 3 inches thick on the floor of the muffle. It is first heated to redness, and then more gently, with the muffle door open, to oxidise the mass thoroughly before sublimation. The operation is completed in 11 or 12 hours.

*Condensation of the oxide.*—The vapours passing off in the roasting are carried through chambers so arranged that the gases come in contact with a very large condensing surface passing through a series of chambers before escaping into the air. At the Devon Great Consols and other large works, the chambers are made of thin brickwork covered with iron plates to assist the cooling of the gaseous oxide. The ores, before calcination, are dried over iron plates on the condensers.

These chambers are cleared at intervals, some every fortnight, those at Silesia once in two months. Two sets of chambers are frequently used, so that one set may be working while the other is being cleared.



The oxide produced by all processes except that of the muffle is known as 'arsenical soot' and is impure, containing carbon and sulphur compounds; when so mixed it is of a dark-grey colour and requires to be resublimed.

The condensing chambers connected with the muffles in Silesia—are in a lofty building called the 'poison tower' (*Giftthürme*). The gases traverse, by a sinuous course, a series of chambers, depositing the finest product in the lower ones, that in the upper chambers containing sulphur. The chambers are cleared about every two months, and contain about 25 tons of white arsenic ('poison flour' or *Giftmehl*). Being comparatively pure, it does not usually require refining, but may be at once converted into arsenical glass. The workmen engaged in

clearing the chambers are clothed in leathern garments with glazed apertures for the eyes, and wear wet cloths over their mouths and noses to absorb the irritating fumes. It is stated at Salzburg that only 'arsenic eaters' can perform this work continuously.

*Refining or resublimation.*—For this purpose a reverberatory furnace is used, which is usually much shorter than that in which the calcination is performed. The arsenical soot is charged from the top and paddled down through doors at the side, more being added as it sublimes. The fuel used is smokeless, usually a mixture of anthracite and coke.

The sublimate is collected in chambers similar to those already described. It is white, glistening, and minutely crystalline. It is ground

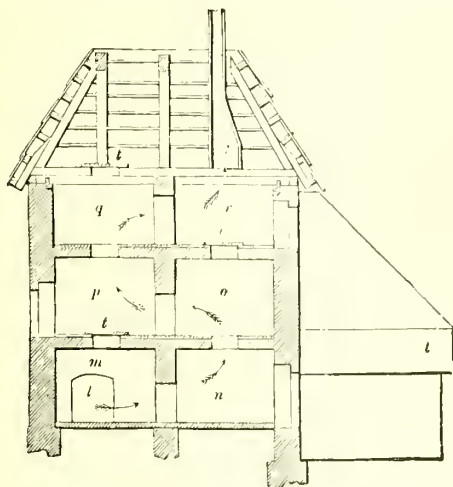


FIG. 5.—VERTICAL SECTION OF 'POISON TOWER.'

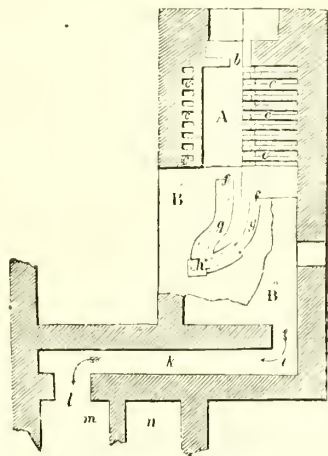


FIG. 6.—GROUND PLAN OF FURNACE.

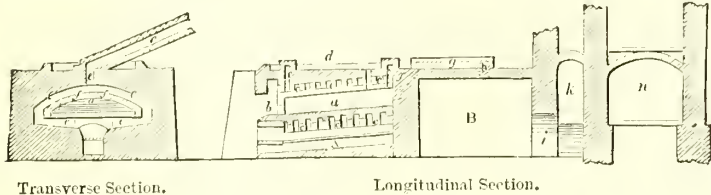


FIG. 7.—SUBLIMING FURNACE.

between millstones, and is thence fed into kegs from a hopper through a leathern hose which fastens to the top of the cask and prevents any escape of the powder.

*Arsenic glass*, or vitreous white arsenic, is prepared by volatilisation of the powder under slight pressure. For this purpose, at Swansea, a cast-iron pan is used 2 ft. in diameter and surmounted by a bell 2 ft. 6 in. high. The pan is heated to a cherry red and about  $\frac{1}{4}$  cwt. of refined white arsenic introduced through an opening in the top of the bell, which is then closed with a plug. In about 2 hours the whole has evaporated and condensed on the bell as a transparent glass; more white arsenic is then introduced and condensed, until after about 24

hours the glass has reached a thickness of about 1 inch. The later charges, owing to the condensing surface being hotter, require about twice as long to condense as the first.

At Silesia the subliming pots are deeper and of greater capacity; they are surmounted by iron drums and conical caps, which condense the 'glass' and open into condensing chambers. The temperature is carefully regulated. The arsenic glass produced amounts to about 92 p.c. of the 'flowers' used.

White arsenic is obtained in immense quantities in the calcination of tin ores in Cornwall and Devon. During the ten years 1877–1888, of a total quantity of 63,338 tons of white arsenic, of the value 430,232*l.*, produced in the United

Kingdom, 28,754 tons of refined white arsenic powder were extracted by the Devon Great Consols Company at Tavistock.

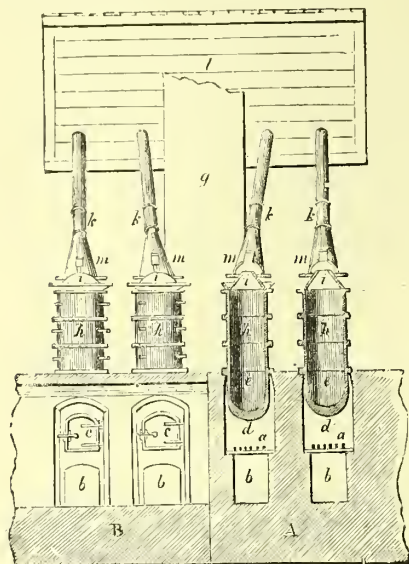


Fig. 8.

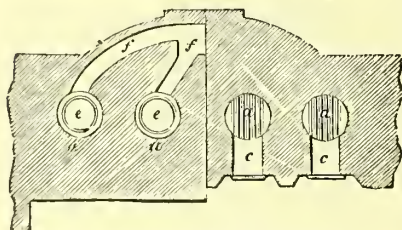


Fig. 9.—REICHENSTEIN FURNACES.

#### Analyses of arsenic powder and arsenic glass.

(1) Powder from Altenburg, from the condenser of a tin roasting furnace, near the furnace end (Lampadius).

(2) Do. from further end of condenser (Lampadius).

(3) Do. from Oberschlema (Lampadius).

(4) Arsenic glass from Andreasberg (Streng).

	(1)	(2)	(3)	(4)
Arsenious oxide . . .	90.1	95.85	94.31	98.2
Arsenious sulphide . . .	2.05	0.32	1.03	—
Bismuth . . . . .	—	—	0.25	—
Sulphur . . . . .	0.73	0.71	0.50	—
Ore dust . . . . .	5.51	2.05	3.05	—
Fume . . . . .	1.04	0.74	0.16	—
Antimonious oxide . . .	—	—	—	1.68

#### Properties and uses of arsenious oxide.—

White arsenic occurs in the amorphous or glassy form, and in two crystalline modifications:—(1) the octahedral or common form, and (2) in trimetric prisms, occasionally found in sublimates; this form is converted into the octahedral variety when heated or boiled in water.

The amorphous form is transparent when first prepared, but becomes opaque when exposed

to the air, especially when damp diminishing slightly in specific gravity and forming the crystalline oxide. The action commences at the outside, so that even after a considerable time a piece is frequently found with a transparent nucleus. The vitreous form may be kept in a sealed glass tube unchanged for years.

The vitreous form, according to Buchner, is soluble in 108 parts of cold water, while the opaque form requires 355 parts; the solubility of an ordinary piece is therefore doubtful, depending on the amount of change it has undergone. It is very soluble in glycerine, and is stated by Jackson to form *glyceryl arsenite* (C. N. 49, 258).

On making a strong solution of the *vitreous* form in dilute hydrochloric acid by dissolving 3 parts in a mixture of 12 hydrochloric acid and 4 water, and slowly cooling, it is deposited in the octahedral form, each crystal as it falls producing a flash of light (H. Rose). If these crystals be redissolved or if the opaque form be used, no light is produced on crystallising, that phenomenon appearing to depend on the change of the amorphous into the crystalline form at the moment of crystallisation.

At about 193° arsenious oxide softens and sublimates without fusion; it fuses under pressure: its vapour is colourless and odourless. It is acid to test papers, but does not appear to form true arsenious acid on solution in water.

Arsenious oxide is a powerful febrifuge, being sometimes efficacious when quinine has failed. It is highly poisonous, 2 or 3 grains being a very dangerous dose. When used habitually, however, comparatively large quantities may be taken with impunity. The inhabitants of Styria eat it under the name of 'hydrach' to increase their endurance. Many authentic cases are recorded of 6 grains and upwards being taken without ill effect. Arsenic eaters are stated to be fresh complexioned, with a tendency to stoutness, to be long lived, but to die suddenly. The workmen engaged in the manufacture of dyes where arsenic acid is used have been observed to have this tendency to stoutness (*v. Roscoe*, Mem. of Lit. Phil. Soc. Manchester, 1860). Arsenic is frequently the cause of poisoning. In the years 1876 to 1880, in 1,581 cases of poisoning, 67 deaths were traced to arsenic, which would correspond to about 175 cases, or about 12 p.c. of the whole. In cases of death from poisoning, the greater part of the arsenic appears to be contained in the liver and intestines; of the bones, those of the pelvis and neighbouring vertebrae appear to contain most.

In manufactures, arsenious oxide is used for the reduction of indigo blue, and for reducing nitrobenzene to aniline; in glass-making to remove the colour produced by the lower oxides of iron; in enamelling; in calico-printing; as a constituent of white fire in pyrotechny; for the prevention of boiler incrustations (40 parts white arsenic to 9 carbonate of soda); in the manufacture of arsenic acid; and of fly and rat poisons; and in the manufacture of a large number of pigments, arsenic being found in green, blue, pink, white, brown, and other colours. As a preservative it is thrown into the holds of ships to prevent vegetable decomposition; as a wash for walls in India to prevent insect ravages; to prevent smut in wheat; and with carbonate of

soda as a wash for sheep; and in arsenical soap, for preserving skins.

Arsenious oxide is employed in the fixation of aniline colours, especially of aniline blue. It is used principally for preparing steam colours, either as a solution in glycerine containing 4 lbs. of the oxide to 1 gallon of glycerine, under the name 'arsenic and glycerine standard,' or as sodium arsenite, dissolved in sodium carbonate or borate.

In medicine it is used as Fowler's solution, which contains 4 grains of the oxide (in the form of sodium arsenite) in each ounce of fluid. In India it has been used as a cure for hydrophobia and serpent poisoning. In veterinary surgery it is largely used as a tonic, to eradicate worms, and for improving the coats of horses.

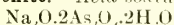
It occurs, either as an impurity or as an adulterant in a large number of commercial products. Besides the ordinary commercial compounds in which arsenic is expected to be present, it has been found in caustic soda, potassium chlorate, commercial glucose (Clouët and Ritter) and in wine free from artificial colouring matter (traced to sulphuric acid used in purifying the casks). Dr. Tidy found about 38 p.c. of arsenious oxide in some 'violet powder' which had caused the death of at least two children (Lancet, Aug. 21, 1878).

For a statement of the amount of arsenic in the varieties of pyrites, and of its distribution in the preparation of sulphuric acid and alkali, v. H. Smith, P. M. [4] 41, 370; C. N. 26, 176; and C. Hjelt, D. P. J. 225, 174-181.

Fresenius finds that the arsenic in many chemical glasses is removed by alkaline, but not by acid liquids; the bearing of this on judicial investigations is important.

The commercial article is frequently adulterated with gypsum, chalk, &c.; these may easily be detected by heating a little on a knife, when they will remain after the oxide has volatilised.

#### Sodium arsenite. *Acid sodium arsenite.*



is prepared by dissolving arsenious oxide in a solution of caustic soda or sodium carbonate, and evaporating the solution. The neutral salt,  $\text{Na}_2\text{O} \cdot \text{As}_2\text{O}_3$ , is formed by boiling this compound for some time with sodium carbonate, and washing the residual salt with alcohol (Pasteur).

Potassium arsenite is prepared in a similar manner.

Sodium arsenite is used as a substitute for dung in dyeing, but is not so reliable as the arsenate. It enters into the composition of all preparations in which arsenious oxide is dissolved with sodium carbonate.

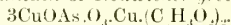
An arsenite of chromium and iron is used as a green pigment in wall papers.

**Scheele's Green.** *Arsenite of copper. Hydrocupric arsenite.*  $\text{CuHASO}_3$ .

According to Scheele's method, 11 oz. arsenious oxide are gradually added to a solution of 2 lbs. potassium carbonate in 10 lbs. boiling water; this is filtered and poured into a solution of 2 lbs. copper sulphate in 30 lbs. water, so long as a grass-green precipitate falls. The precipitate is thrown upon a filter cloth, washed with warm water, and dried gently with the production of about  $1\frac{1}{2}$  lbs. of the pigment.

Scheele's green is a pulverulent, fine light-green colour, formerly largely used in calico-printing and for wall papers. It is, however, much less used at the present time. It dissolves entirely in excess of alkali and in acids.

**Schweinturth green.** *Imperial green. Emerald green. Mitis green. Aceto-arsenate of copper* (when mixed with gypsum or heavy spar known also as *Mountain or Newwieder green*).



Five parts of verdigris (basic copper acetate) are made into a thin paste with water and added to a boiling solution of rather more than 4 parts arsenious oxide in 50 parts water; the solution is kept boiling during the mixture. If a yellow-green precipitate falls a little acetic acid is added, and the solution boiled a few minutes longer; the precipitate becomes crystalline and soon acquires the characteristic green colour.

A very fine product is prepared by the following method:—Boiling, concentrated solutions of arsenious oxide and copper acetate are mixed in such proportions that equal weights of the two substances are present when a bulky olive-green precipitate falls; an equal bulk of cold water is then added and the mixture placed in a flask which it fills to the neck, thus preventing any pellicle which may form on the surface from falling through the liquid and causing a premature crystallisation. The colour under these circumstances takes two or three days to perfect, the beauty of the product being much increased by slow formation. The workmen engaged in the preparation of this pigment do not appear to be injured by it. In contact with organic matter it is, however, liable to change. Bischoff (Fr. 23, 117) states that micro organisms and fungi act on compounds of arsenic, producing arsenuretted hydrogen, and Fleck, Sommschein, and others have conclusively shown that this gas is frequently present in the air of rooms with arsenical wall-paper. By the action of damp and mould on paper coloured with this pigment a peculiar odour is frequently produced which appears to be due to the formation of propionic acid.

**Arsenic oxide.** *Arsenic acid, Arsenic pent-oxide, Acide arsenique, Arsensäure, Acidum arsenicum.*  $\text{As}_2\text{O}_5$ .

Produced when arsenious oxide is acted upon by an oxidising agent.

On the large scale 4 parts white arsenic are gradually added to 3 parts nitric acid of not less than 1.35 sp.gr. in a vat capable of holding from 65 to 70 kilos of white arsenic. Great heat is produced and the evolved fumes are passed over coke moistened with water, whereby about two-thirds of the nitric acid is recovered. In 24 hours a syrupy liquid is formed, containing a small quantity of arsenious oxide, which may be oxidised with a little more nitric acid.

Kestner performs the oxidation in large glass flasks, the nitrous fumes being passed through lead pipes and condensed in leaden chambers.

Arsenic oxide has also been prepared by suspending arsenious oxide in water, passing a current of chlorine through the liquid and evaporating the solution thus produced.

It is a deliquescent solid fusing at a dull red heat, of acid metallic taste and acid reaction.



It dissolves in 6 parts cold and in 2 parts hot water. A cold, strong solution blisters the skin. Arsenic oxide and its salts are less poisonous than the corresponding arsenious compounds. It is largely used as an oxidising agent in the preparation of rosaniline or fuchsine.<sup>1</sup> It is also substituted for tartaric acid in calico-printing. Weiler has recently patented a process for the separation of aniline and paratoluidine by means of arsenic oxide (Eng. Patent, 1883, 3,113).

**Sodium arsenate.** *Hydric disodic arsenate*; 'Dung salt.'  $\text{Na}_2\text{HASO}_4$ .

This salt is produced as a by-product where arsenious acid has been used in the reduction of indigo blue or in the preparation of aniline.

It is prepared by saturating arsenious oxide with crude soda ash, drying, and deflagrating with sodium nitrate in a reverberatory furnace.

Arsenate of soda is largely used in calico printing as a substitute for dung, its feebly alkaline properties rendering it useful for that purpose.

*Arsenate of iron* is an amorphous green powder containing 33.6 p.c. arsenic.

**Arsenic sulphides.** Arsenic forms three well-defined sulphides,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ , and  $\text{As}_4\text{S}_6$ , the two former occurring naturally. A large number of other sulphides of indefinite composition also exist.

**Realgar.** *Disulphide of arsenic.* *Ruby sulphur.* *Roths rauschgelb.* *Roths Schwefel.* *Sulphur rouge.* *Orpin rouge.* *Risigallo.* *Sandaraca.*  $\text{As}_2\text{S}_4$ .

Prepared by fusing together arsenic and sulphur or orpiment in the proper proportions. On the large scale it is obtained by distilling a mixture of arsenical ores, such as arsenical and iron pyrites, with sulphur or with the sulphide of arsenic precipitated in the purification of sulphuric acid.

The mixture should contain about 15 p.c. arsenic and 26 to 28 p.c. sulphur; it is placed in flask-shaped earthenware retorts, holding about 60 lbs. when two-thirds full, which are connected with similar receivers. The retorts are gradually heated to redness and kept so for 8 to 12 hours. The crude realgar should be compact, dark, and rich in arsenic; if sulphur be in excess it is friable and light red. It is re-melted rapidly in cast-iron pans with the requisite amount of sulphur or arsenic, or with realgar of poorer quality. The mass is cleared of slag

<sup>1</sup> According to C. Winkler (C. C. 1876, 651) the following process has been successfully adopted for the recovery of aniline from the mother liquors obtained in the conversion of aniline into fuchsine. The liquor, which contains the arsenic as sodium arsenate, is neutralised with soda, and the colouring matter which separates is removed. Excess of soda is then added and the strongly alkaline liquid is evaporated until a skin forms on the surface, and is added, with constant stirring, to a mixture of 30 kilos. powdered limestone and 25 kilos. coal dust or coke for each 100 kilos. of the saturated solution of sodium arsenate.

A reverberatory furnace is used, having an upper and a lower sole, the lower one being heated to a moderate redness. The upper sole, having a temperature of about 100°, is charged with 500 kilos. of the mixture, which when dry is allowed to fall upon the lower sole, the air being then almost excluded from the furnace. The fumes of metallic arsenic may be condensed as such, or may be burned as they leave the furnace, the arsenious oxide being condensed in the usual way.

From the residues the sodium carbonate may be re-obtained by lixiviation, while the limestone may be used several times.

and heated until quite fluid, and until a small quantity shows the proper appearance on cooling. It is then poured into conical sheet-iron moulds.

Greater care is necessary in the preparation of realgar than of orpiment, and an assay is frequently made to ascertain the exact proportions required before the final melting.

It is hard and brittle, generally opaque, with vitreous conchoidal fracture, orange or hyacinth red in mass and orange red in powder. Its specific gravity is 3.4 to 3.6, and its usual composition is arsenic 75, sulphur 25. It volatilises easily before the blowpipe with a smell of garlic and burning sulphur, is insoluble in water or hydrochloric acid, but soluble in alkaline sulphides.

Realgar is a constituent of blue fire and of 'White Bengal fire,' which is used as a signal light, and consists of realgar 2, sulphur 7, potassium nitrate 24.

The finest variety, especially that which occurs native, is used as a pigment by artists.

**Orpiment.** *Operment.* *Gelbes Rauschgelb.* *Risigallum.* *Auripigmentum* (of which its usual name is a corruption). *Yellow Sulphide of Arsenic.*  $\text{As}_2\text{S}_3$ .

This sulphide is formed as a yellow precipitate when sulphuretted hydrogen is passed through a solution of arsenious acid in hydrochloric acid.

Schultze (J. Pr. 25, 431) considers that another form of the trisulphide exists which is soluble in water.

On the large scale it is prepared by subliming sulphur with arsenious oxide, 2 parts of arsenious oxide and 1 part sulphur being a common proportion; the colour of the product is lighter when less sulphur is used.

According to R. Wagner a very fine colour may be produced as follows:—2 parts finely ground barium sulphate are calcined with 1 part powdered charcoal or other carbonaceous matter, and the product is pulverised, mixed with 1 part ground orpiment, boiled in water and filtered. The solution, containing a sulpharsenite of barium, is precipitated by the addition of sulphuric acid. By the addition of a suitable amount of barium chloride before precipitation the pigment may be correspondingly lightened in colour.

Orpiment is insoluble in water but very soluble in alkaline sulphides. It was formerly much used as a pigment under the name of King's Yellow but now is largely replaced by chrome yellow. The lighter varieties contain as much as 80 to 90 p.c. of arsenious oxide, and are consequently very poisonous. The darker varieties contain from 1 p.c. to 15 p.c. of the oxide and from 0.2 to 3 p.c. non-volatile matter. It is used in pyrotechny, and the finer kind, especially the mineral, is made into pigment for artists.

It was formerly used as a deoxidising agent in the reduction of indigo blue, and in ammoniacal solution in silk dyeing. A mixture of 9 orpiment and 1 quicklime made into a paste with water is used under the name of 'Rusma' for removing hair from skins, but is now generally replaced by the solution of sulphide of lime prepared from the spent lime of gasworks.

**Arsenic pentasulphide**  $\text{As}_2\text{S}_5$ . The existence of this sulphide in the free state has, until

recently, been somewhat doubtful. Berzelius in 1826 stated that it was formed when sulphuretted hydrogen is passed through a moderately concentrated solution of arsenic acid, but the precipitate was generally considered to be a mixture of the trisulphide and sulphur. Bunsen in 1878 showed that it was produced on passing a rapid current of sulphuretted hydrogen through a hot hydrochloric acid solution of an alkaline arsenate, and his results were confirmed by McCay in 1887. Still more recently, Brauner and Tomiček (C. J. 1888, 147) have made a quantitative investigation of the question, and have also confirmed Bunsen's statement. They find that from a solution of alkaline arsenate containing excess of hydrochloric acid, sulphuretted hydrogen precipitates the *pure* pentasulphide both in hot and cold solution, but much more rapidly in the former.

Arsenic pentasulphide is totally insoluble in water, alcohol, and bisulphide of carbon. The dry substance, on rubbing in a mortar, becomes strongly electrical.

**Arsenic chloride.** *Butter of arsenic.* *Caustic oil of arsenic*  $AsCl_3$  is produced by the action of chlorine on arsenic; by distilling arsenic with mercuric chloride; and by distilling arsenious oxide with strong hydrochloric acid. It is a colourless, oily liquid, of sp.gr.  $2.205^{\circ}$ , boiling at  $130^{\circ}C$  (Thorpe).

The chloride and iodide are used to a slight extent in medicine.

Arsenic forms a large number of organic compounds with various organic radicles. Of these kakodyl or arsenic methide may be mentioned. It has a very characteristic disagreeable odour, and is produced when arsenious oxide is heated with sodium acetate.

(For other compounds of Arsenic *v.* WATTS' DICTIONARY OF CHEMISTRY.)

**ARTOCARPUS BARK.** The inner bark (bast) of the bread-fruit tree (*A. incisa*) is used by the South Sea Islanders for making ropes and clothing. According to Moeller (D. P. J. 231, 463), this fibre would probably be a very useful one. It can be obtained in large quantities.

**ARUM MACULATUM.** The common arum, 'wake robin,' or 'lords and ladies,' 'cows and calves,' formerly known as 'abron' janus, 'ramp,' 'starch wort,' contains a starch which was made into a kind of arrowroot in the Isle of Portland, and was the active ingredient of 'Portland powder,' a so-called specific for gout. Occasionally sold in Paris as a cosmetic, under the name of *poudre de Cypre*.

*A. campanulatum* is used in India as a vegetable, and also in medicine, as are other of the Arums. Many of the Aroideæ act as poisons, their toxic action being due apparently to the irritation induced by the raphides contained in the cells (Pedler and Warden, Journ. Asiatic Soc. of Bengal, 57, 2, 103).

**ASAFŒTIDA** *v.* GUM RESINS.

**ASARUM CANADENSE, OIL OF.** *Wild ginger oil.* Is used by perfumers and soap-makers. It yields on fractioning a body isomeric with oil of turpentine, a substance having the composition of Borneo camphor, and an oil of an intense blue colour (Ph. [3] 11, 430).

*Asarum europæum* or *Asarabacca* contains asarone  $C_{20}H_{26}O_3$ , asarite, and a yellow

asarum oil. The leaves and root are used as an emetic and as a counter-irritant. It is the basis of many cephalic snuffs (Coolcy).

**ASBESTOS** from *ἀσβεστος*, unconsumable. (*Asbeste*, Fr.; *Asbest*, Ger.) When the fibres of certain varieties of amphibole are so slender as to be flexible, the substance is called asbestos, or amianthus. Asbestos is found in Piedmont, Savoy, Salzburg, the Tyrol, Dauphiné, Hungary, Silesia, in the United States, Canada, in the Umsinga division, South Africa; at St. Kevern, in Cornwall, at Balta, Shetland, and at Shiness, Sutherlandshire. A large deposit of asbestos has been found at Gundagai, New South Wales, and is now being mined. Asbestos is manufactured into fabrics for curtains, fireproof clothing, and for filtering acids; into ropes, sheets, and rings, for closing flanges, for packing small cylinders, and other purposes. It is also used in the manufacture of fireproof paint. White (C. N. 44, 65) suggests the use of asbestos stoppers for combustion tubes. The purest and most flexible asbestos is that known as *Bostonite*, found in Canada. For its manufacture and use as a paint see S. C. I. 1, 355; 2, 351; into tissues, &c., see S. C. I. 1, 311, 450; 3, 517; 4, 284, 530. Analyses of asbestos will be found in the J. 33, 1,463; 36, 1, 892.

Common asbestos occurs in fibres of a dull greenish colour, and of a somewhat pearly lustre. It is common in the serpentine formation at the Lizard Point in Cornwall.

Mountain Leather or Mountain Paper is found at Waulock Head. Its fibres are not parallel like ordinary asbestos, but interwoven.

Elastic Asbestos or Mountain Cork floats on water; and in appearance and feel is not unlike common cork.

Mountain Wood or Ligniform Asbestos is usually found massive and of a brown colour, having much the appearance of wood.

**ASDUANA** *v.* BRIDELIA BARK.

**ASEPTOL.** Trade name for *o*-phenol sulphurous acid  $C_6H_4(OH)SO_3H$ . It is a thick reddish fluid, of 1.45 sp.gr., having a faint odour like phenol. It is an antiseptic, but does not possess the poisonous action peculiar to phenol, and is therefore recommended for surgical and ophthalmic operations (C. C. 1884, 720; S. C. I. 3, 530).

**ASFRAX** or **TRAYAMANA.** An Indian drug, consisting of the flowers, flowerstalks, and immature fruit of a species of *Delphinium*. Used in Bombay as a medicine, and as a yellow dye for silk (Dymock, Ph. [3], 8, 161).

**ASH** in its widest sense may be taken to mean the inorganic matter contained in animal or vegetable substances. Usually it is understood to denote the mineral matter left on the burning or *incineration* of such substances. It consists usually of the carbonates, sulphates, sulphides, silicates, and phosphates of potassium, sodium, calcium, magnesium, manganese, and iron. Aluminium, zinc, and copper, and also fluorine, bromine, and iodine, together with minute quantities of other elements, are not unfrequently met with. The inorganic matter obtained by combustion of the animal or vegetable matter frequently differs both in amount and in proximate composition from that originally present in the unburnt substance. At the high temperature of

burning some of the mineral constituents may be volatilised, or be mechanically carried away by the gases which may be evolved, and changes in the proximate nature may be induced either by the heat itself, or by the action of the heated carbonaceous substances. Thus chlorides are apt to be lost by volatilisation, or a portion of the hydrochloric acid may be expelled by silica or phosphoric acid, or by the action of organic acids. Nitrates and salts containing organic acids are converted into carbonates, sulphates are reduced to sulphides, and the cyanides and cyanates are formed by the action of alkaline carbonates upon nitrogenous organic matter. Hence, in many cases, the analysis of an ash very incompletely represents the mode of arrangement of the various inorganic constituents in the unburnt substance.

Analyses of ashes have, however, afforded important information concerning the nature and distribution of mineral matter in organised bodies, and they have enabled us to determine what are the essential inorganic constituents of plant and animal food. The plant obtains these constituents by the action of the roots upon the soil, partly by a sort of digestive action on the insoluble substances and partly by the rise of solutions of the salts in the capillary vessels. Mineral matters, such as potash and phosphoric acid, are employed in the formation of new tissue;

calcium salts and silica are deposited as an incrustation on tissues already made, whilst the soluble salts still remaining in the sap, and which would otherwise gradually accumulate, are eliminated either by the action of rain or by diffusion back into the soil through the agency of the roots. Although plants appear to exercise a certain selective action on the mineral matter of a soil, retaining, for example, potash whilst excluding soda, they manifest a very considerable power of adaptation, and accordingly plants of the same kind when grown on different soils may exhibit very wide variations both in the amount and nature of the mineral matter they contain. The nature of the ash of certain kinds of plants is, however, very characteristic. Thus, the ash of the cereals and the equisetums contains relatively large quantities of silica, whilst that of the lycopods is remarkable for the amount of alumina—otherwise but sparingly met with in the vegetable kingdom—which it contains. The various algæ, and many plants growing on the sea-shore, especially of the genus *Salsola*, contain large quantities of soda, and certain of these were formerly used as sources of supply of sodium carbonate.

The following table, compiled from Wolff's *Aschen Analysen*, will serve to show the nature of the ash of a number of important animal products:—

		Ash in 100 pts. dry subst.	100 parts of ash contain—								
			K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	Cl
Blood (human)	.	—	26·6	24·1	0·9	0·5	8·2	8·8	7·1	—	30·7
„ (ox)	.	3·77	7·6	15·0	1·1	0·6	9·4	5·3	3·1	0·8	34·4
Milk (human)	.	0·49 <sup>1</sup>	33·8	9·1	16·7	2·2	0·2	22·7	1·0	—	18·4
„ (cow)	.	0·72 <sup>1</sup>	24·1	6·1	23·2	2·6	0·4	28·0	1·3	—	13·5
Flesh (mammals)	.	1·32	7·0	10·1	2·4	3·2	0·4	41·2	1·0	0·7	4·7
„ (fowls)	.	—	36·9	18·7	3·3	4·2	—	36·4	—	—	8·1
„ (fish)	.	—	21·8	14·9	15·2	3·9	—	34·5	—	—	11·4
Hen's egg (without shell)	.	3·48	17·4	22·9	10·9	1·1	0·4	37·6	0·3	0·3	9·0
„ „ (white)	.	4·61	31·4	31·6	2·8	2·8	0·6	4·4	2·1	1·1	28·8
„ „ (yolk)	.	2·91	9·3	5·9	13·0	2·1	1·7	65·5	—	0·9	1·9

<sup>1</sup> In fresh substance.

**ASPEROLITE.** A copper silicate from Ta-gilsk, containing 31·94 SiO<sub>2</sub>, 40·81 CuO and 27·25 OH<sub>2</sub>. Sp.gr. 2·306 (Hermann, J. pr. 97, 352).

**ASPHALT.** *Compact bitumen, Mineral pitch, Jews' pitch, Bitumen of Judæa.* (*Judenpech, Erdpech, Bergpech*, Ger.; *Goudron minéral*, Fr.) A name given to the solid varieties of bitumen. In its purest form asphalt presents the appearance of a black or brownish-black solid substance, possessing a bright conchoidal fracture. It melts at 100°, burning with a brilliant flame and emitting a bituminous odour. Sp.gr. 1·0 to 1·08. Asphalt is insoluble in alcohol and water, soluble in about five times its weight of naphtha, and in benzol. It is dissolved by alkalis and alkaline carbonates.

By dry distillation a yellow oil, Asphalt oil, is obtained. It consists of hydrocarbons mixed with a small quantity of oxidised matter. It begins to boil at 90°, but the boiling-point gradually rises to 250°. The portion boiling below 200° has the sp.gr. 0·817 at 15°; that above 200° has a sp.gr. of 0·808 at 15°. Both

portions gave by analysis about 87·5 p.c. carbon, 11·6 p.c. hydrogen, and 0·9 oxygen, which is nearly the composition of oil of amber (Vöckel, A. 88, 139). Nitric acid converts it into a resin, having the odour of musk and the taste of bitter almonds.

Boussingault obtained from the asphalt of Bechelbrunn a pale yellow oil, *Petrolene*, having a faint taste and bituminous odour of sp.gr. 0·891 at 21° C., and boiling at 280° C.

By heating asphalt to 250° for 48 hours the volatile oils are driven off; a black solid substance, *Asphaltene*, is obtained. It becomes soft and elastic about 300° C.

The purest asphalt is found on the shores of the Dead Sea and in the pitch lakes of Trinidad and Mexico. Rocks more or less impregnated with bitumen, to which the name earthy or crude asphalt is given, are found at the Poldice mines, Cornwall, near Matlock, Derbyshire, at Haughmond Hill, Shropshire, at the Hotwells, near Bristol, in the limestone near Glasgow, the freestone near Edinburgh, and



generally throughout the Orkneys. Large deposits occur also at Seyssel, Dépt. de l'Ain, at Bechelbunn and Lobsann, Lower Rhine, at Bastennes and Dax, in the Dépt. des Landes, in the Val de Travers, Neuchâtel and other places.

Asphalt is separated from the minerals with which it is associated either by melting the mass, allowing the earthy matters to subside and removing the bitumen, or by boiling with water, which causes the bitumen to run out in the melted state; or by the action of hydrochloric acid, which dissolves the calcium carbonate and leaves the asphalt; or with oil of turpentine, which dissolves out the bitumen. Murrie (S. C. I. 3, 182) describes the methods used in Italy for the extraction of bitumen from crude asphalt.

The Val de Travers asphalt contains about 20 p.c. of bitumen, and it only requires the addition of 6 to 8 p.c. of mineral or coal tar to convert it into a plastic, workable mastic of good quality for pavements and hydraulic works.

The modern method of laying down asphalt pavement is to first prepare a foundation of concrete, the surface of which is carefully flattened. On this even surface, when thoroughly dry, the melted asphalt is spread with a wooden trowel, and the surface is finally smoothed over. The liquid Val de Travers, Limmern's, and Barnett's asphalts used for this purpose are all mixed with grit or sand, and so present rougher surfaces than those pavings which consist of asphalt alone. Brande (Ger. Pat. 4,993, 1878) mixes ground slag with the asphalt instead of sand.

Another method of paving is to break up the bituminous ore, and heat the fragments till they crumble to powder. A layer of this hot powder, from 16 to 20 inches thick, is laid on the dry concrete and compressed by stamping with hot irons.

*Artificial asphalt, or gas-tar asphalt*, is a mixture of chalk, sand, or limestone with the thick, pitchy residue obtained by evaporating the more volatile portions of gas-tar. The mineral substance must be heated to expel moisture and adhering air, and then added to the strongly-heated pitch.

In addition to the use of asphalt for pavements, water-tight tanks, and coatings for iron tubes used for conveying gas or water &c., it is used in photography, in photo-lithography and photo-engraving, owing to the asphalt becoming insoluble in turpentine after exposure to light. In the latter case copper plates are covered with a thin coating of pure asphaltum, or bitumen of Judæa, dissolved in benzole or chloroform. When dry, the plate is exposed behind a film to bright sunlight for half an hour, and then developed by first softening the soluble portion of the asphaltum with olive oil, to which subsequently a little turpentine is added. As soon as the lines are bare the turpentine and oil must be washed away by the action of water.

Methods for preparing asphalt for paving and other purposes are described by Dugasan (Ger. Pat. 4,999, 1878; D. P. J. 232, 547); Kalibetzer (Ger. Pat. 5,646, 1878); Zadig a. Neuberg (Ger. Pat. 5,678, 1878; D. P. J. 233, 490); Clark

(Eng. Pat. 8,036, 1884; S. C. I. 5, 183); Kettmann (Eng. Pat. 12, 425, 1884; S. C. I. 4, 675); Richter (Siefenseid Zeit. 23, 272; S. C. I. 2, 474).

Native asphalt can be distinguished from artificial asphalt by extracting with carbon disulphide, filtering, evaporating to dryness, and heating the residue till it can be ground to a fine powder; 0.1 gram is treated with 5 c.c. of fuming sulphuric acid for 24 hours, and is then mixed, with continuous stirring, with 10 cc. of water. If pitch or coal tar be present, the solution will be of a dark brown or blackish tint; if not, the solution will be of a light yellow colour (c. Pitch).

**ASPHODEL.** The bulbs of *Asphodèle de Sardaigne*, of *Asphodelus racemosus*, and other species of the same genus, are said to contain a fermentable substance from which alcohol may be prepared. By drying and coarsely grinding the bulb Landerer obtained a powder which, mixed with water, formed a strong glue. Badoil and Lienders obtain tannin from the pulp left after the extraction of the alcohol.

**ASPIDIN** v. FILIX-MAS.

**ASPIDOSAMINE** and **ASPIDOSPERMINE** v. VEGETO-ALKALOIDS.

**ASPIRATORS.** Aspirators are used to draw air or other gases through any apparatus connected with them, and were probably first employed by Brunner in his analyses of air, 1830–1840. When a vessel is emptied of liquid, air must enter to take its place, and the common aspirator, in its various forms, is a vessel with two openings, the lower to serve as outlet for the water or liquid, and the upper as inlet for the air or gas to be aspirated. With suitable fittings a syphon may be used instead of the lower opening, or the apparatus may be modified into a bell-jar standing over a basin or large jar, the air being drawn in through the neck of the bell-jar. This is Mohr's aspirator, which is sometimes poised like a gasholder to facilitate filling and emptying of the bell-jar.

From their introduction, aspirators were used not only to draw in gases through apparatus and reagents employed, at a regulated rate, but also to measure the gases so manipulated by simply measuring or weighing the liquid run out of the aspirator. For approximate readings aspirators of glass may be graduated, and those of metal may be provided with gauge glasses.

Numerous forms of the simple aspirator have been invented by Brunner, Regnault, Mohr, and

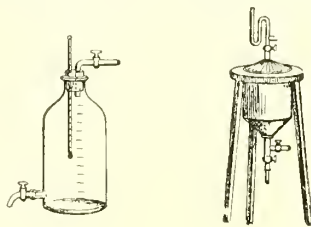


FIG. 1.

FIG. 2.

others. Fig. 1 is perhaps the form in most frequent use, and is generally of glass, plain or graduated. Fig. 2 is a very convenient form, described by Clemens Winkler (Industrie-Gase,

1877, 39-41) constructed of zinc plate and supported on a wooden tripod. The second tap below, on the side tube, is useful in filling the aspirator with water. Fig. 3 is the form often used in testing the gases from chemical works. It is simply a cubical or rectangular box made of sheet lead, with a graduated gauge glass, and can be opened at *a* to fill it with water.

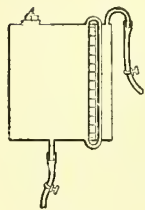


FIG. 3.

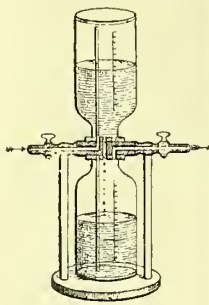


FIG. 4.

*Double aspirators.* In short operations the simple aspirator requires no refilling nor special attention after the taps are adjusted. To obviate the inconvenience of stopping to change or refill that would be necessary in longer operations, Brunner, Boisgiraud, Dancer, Muencke, and others have contrived double aspirators so connected that each vessel is alternately above and below, and one or other always ready for use. The aspirating bottles may be mounted on a common axis as in Dancer's swivel aspirator, fig. 4 (C. N. 1864, 10, 295). These swivel aspirators are very convenient, but the difference of water-level in the two bottles is not under the control of the operator and varies between the height of one bottle and a very small minimum.

Figs. 5 and 6 show an arrangement devised by the author, which has certain advantages. The bottles *a* and *b* are connected as shown, being raised and lowered alternately. The four-

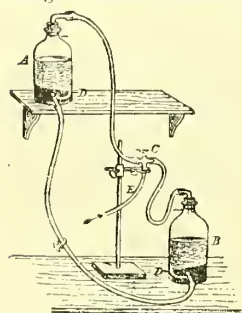


FIG. 5.

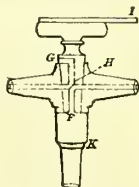


FIG. 6.

way tap *c* (shown larger in fig. 6) has its index *i* turned towards the upper bottle in aspirating and towards the lower bottle in blowing. It is made from a good gas tap by boring up the centre of the plug at *r*, leading out the hole at *g*. A small piece of metal *u* is then fitted and soldered diagonally where the holes cross, a piece of tubing *k* soldered on to the socket of the tap, and an index *i* above the plug.

Paraffin wax is used to adjust the bottles for exact measurement, and to obtain a fine adjustment below at *b*, as well as above, by a mark on the neck of the bottle. The proper quantity of melted wax is run through a wide tube into the warm bottle slightly tilted. A passage from the tubulure to *b* at the side of the bottle is secured by pushing an indiarubber tube through the tubulure and fixing it in the proper position before the wax is run in, and after the wax is quite solid this tube is drawn out. The passage should be curved, so that on emptying the bottle of water the water runs out to the mark at *b*. The bottles are then adjusted by weighing their content of water between the marks and adding or removing paraffin, till at the standard temperature and pressure they hold the exact quantity of water corresponding to the volume required. In successive weighings of bottles so adjusted the differences should not exceed 0.1 gram.

*Constant or automatic aspirators.* Instruments of this class have been invented by Guthrie (P. M. [4] 15, 64) and by Bonny (Winkler's Technical Gas Analysis, trans. by Lunge, 17). In each of them a pipe from the water supply leads a constant stream of water into a vessel, which, when full, is emptied by a syphon, whose tube is of larger size than the supply pipe. The arrangement thus acts on the principle of the intermittent syphon, and the vessel is filled and emptied at regular intervals. In Bonny's instrument these are registered by a simple mechanism, and the total volume passed is known on measuring the volume passed in one operation.

The Sprengel and injector pumps may be used as constant aspirators (*v. FILTER PUMPS*). By means of a collecting box attached below the pumps to allow the gas and water to escape at different levels, the gas may be measured by passing it through a small gas-meter (Davis, S. C. I. 211).

J. Grossman (Winkler's Industrie-Gase, 218) has invented a small mercurial aspirator, on the principle of the Geissler pump, with two reservoirs, which are alternately raised and lowered. It is fitted with registering apparatus.

In testing air and gases from confined places, works, &c., Angus Smith, Davis, and others, have used small pear-shaped aspirators of indiarubber. These are emptied by simply squeezing in the hand. The air escapes by a valve, of which the simplest is a small slit in the rubber connecting-tube, opening outwards like a Bunsen's valve. The rubber recovering its form draws a certain volume of gas through the testing apparatus, and it is easy to ascertain approximately the total volume of gas corresponding to any given number of times the aspirator has been filled. Another larger aspirator of this class is of bellows form, like a concertina, the folding part being of indiarubber. This aspirator is frequently used for filling by displacement jars or bottles with gas to be tested. The common single-barrel air-pump or apparatus, on the same principle, is also applied in this manner as an aspirator.

T. F.

**ASSAYING**, in its widest sense, is the art of ascertaining the proportion of one or more specified constituents in a substance; the term is most generally used in regard to the determination of metals, whether the material under

examination be an ore or metallurgical product or an alloy. As a rule the operations performed are directed to the determination of only a single metal in the sample, constituting a copper, gold, silver, &c., assay, but occasionally, as for example when silver and gold are associated in the same substance, it becomes necessary to determine the proportion of both by what is known as a 'parting' assay.

It would be impossible within the limits of a single article to give any useful account of the entire art of the assayer, covering as it does so extensive a field, and the reader who desires detailed information must be referred to special works, such as Mitchell's *Manual of Assaying*, Balling's *Manuel Pratique de l'Art de l'Essayeur*, or Bruno Kerl's *Metallurgische Probirkunst*.

It will be well to give some brief account of such implements and apparatus as are required for the ordinary work of the assayer, but not, or only on rare occasions, by the analytical chemist.

The ordinary chemical balance can of course be made to serve for much of the work of an assayer, but it is needlessly large and correspondingly slow in action. Moreover, for bullion assaying, and in other cases where the amount to be weighed is either very minute or very valuable, a more sensitive balance is essential. Assay balances are thus very light, and should not be loaded with more than one or two grams in each pan. The best are a justel to turn one scale division with as little as  $\frac{1}{10}$ th milligram. At the present day short beams, about 6 inches in length, are much in vogue, and excellent instruments are made for the use of assayers travelling abroad, which are both portable and accurate.

As a substitute for the balance, Dr. Black suggested a simple appliance which it may be useful to describe; and it has been found possible to dispense altogether with a delicate balance where a *small* bead represents the final result of the assay, and it is known to consist of only one metal, gold for example, by accurately measuring the diameter of the button, and comparing it with a scale previously prepared experimentally. Such a method has been even applied to beads of microscopic dimensions by placing them on the stage of a microscope and measuring by means of a micrometer eyepiece.

Black's extemporised balance consists of a light piece of pine, 12 inches long and 0.3 inches wide at the middle, tapering both in breadth and thickness towards either end. This is supported at its centre on a thin needle fixed transversely on the upper face and resting on narrow brass planes, and it is divided accurately into 10 equal parts on either side of the centre. By placing the piece to be weighed on one side and adjusting the position of one or more of three weights (1 grain, 0.1 grain, and 0.01 grain) on the other side, the weight, not exceeding about 11 grains, can be very approximately ascertained.<sup>1</sup>

One or more ordinary balances should be provided for use in weighing samples and other rough work, but these do not call for special remark.

A few words should, however, be said about the weights, which frequently differ from the

common gram or grain series used in chemical analysis. Much tedious calculation is avoided by so marking the weights that their face value shall give at once the result of the assay. A few examples will at once make this method evident. If the unit weight taken for an assay of gold be marked 1000 and a number of subsidiary weights be provided bearing their several values in terms of this unit, it will only be necessary to weigh the resulting pure gold with these subsidiary weights in order to obtain the millesimal proportion of precious metal in an alloy without resorting to calculation. Again, in assaying silver by precipitation as chloride (*v.* page 212), since 18.817 grains of pure silver are contained in 25 grains of chloride, it follows that if 18.817 grains of an alloy be always taken for assay, and the resulting chloride be weighed out with a series of weights with a unit of 25 grains, which is marked 1000, the subsidiary weights of this series will indicate the result of the assay without calculation. These examples will suffice to show how a series can be arranged for any special purpose, as, for example, a given weight being taken as an ore sample, to ascertain the number of ounces, pennyweights, and grains per ton of ore.

The *furnaces* employed in assaying are of two kinds, muffle and wind furnaces.

The muffle is a small oven of refractory fire-clay, open at the front and usually having an arched top; at the back are small openings for inducing a draught through the muffle (when in position in the furnace). A common form is shown

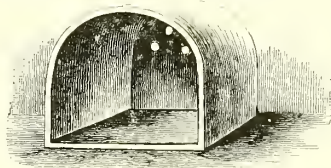


FIG. 1.

in fig. 1. The size varies according to the amount of work usually done at one time, but those used at the Royal Mint, and measuring 37 cm. in length and 19 cm. in breadth outside at the base, may be considered full-sized. The furnace itself is made of wrought iron lined with firebrick, or entirely of firebrick, and is provided with openings for regulating draught, charging with fuel, removing fire bars, &c., when necessary, and the muffle is set to slope from back to front so that all objects on the floor may be clearly visible. The fuel may be charcoal, coke, or anthracite; many forms of muffle furnace also exist in which the heating is effected by gas. A sectional view of a full-sized muffle furnace, as used for gold assaying in the Royal Mint, is shown in fig. 2. Draught is regulated by the damper and by several sliding doors, as well as by a hinged door, through which also fuel is introduced. The mouth of the muffle is closed by the plumbago block, and by a sliding plate.

The wind melting furnace required for assay operations does not demand special description, as it differs in no essential respect from that ordinarily used by the metallurgist.

<sup>1</sup> Faraday's *Chemical Manipulation*, 64.



It must suffice to pass the several small implements and appliances required in rapid review, and the accompanying figures will render de-

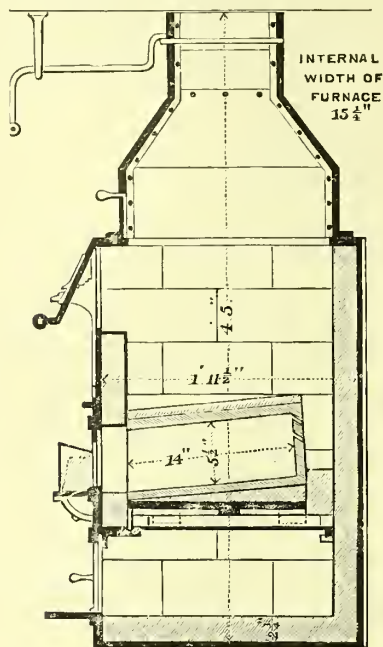


FIG. 2.

tailed description the less necessary. The crucibles generally used are either Cornish, French, or plumbago (*a*, fig. 3), or, in the assay of galena,

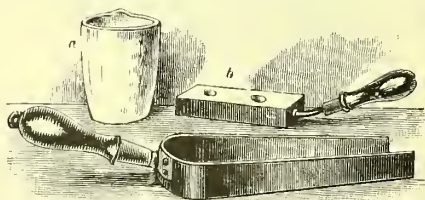


FIG. 3.

wrought iron, and the sizes used vary to suit special requirements. Roasting dishes made of fireclay (*a*, fig. 4) are for the calcination of

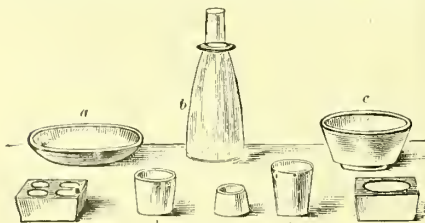


FIG. 4.

ores; scorifiers, *c*, used in the process of scorification (*v. p.* 209); cupels of various shapes and sizes, *d*, are made of compressed bone-ash, and

are required for the assay of the precious metals (*v. p.* 210).

An assay laboratory is also provided with various forms of tongs, scoops, ingot moulds, and furnace implements, such as are shown in figs. 3 and 5.

It will not be necessary to enumerate the reagents required. Their number is not great, and they may be classified under the several heads: Fluxes, Oxidising and Reducing Agents, Sulphurising and Desulphurising Agents, and Solvents.

The above summary has special reference to the requirements of a laboratory for the making of assays by the dry method. Into the several methods of assaying by electrolysis and in the wet way, with one exception in the case of silver, it will not be possible to enter within the limits of this article; they will be found fully described in the several works above referred to.

In what follows it is proposed to describe in some detail the methods usually adopted for the assay of gold and silver, as being the most delicate work in which the assayer can be engaged, and as the assay of the precious metals often involves a knowledge of the assay of lead, it may be convenient to give some account of the methods ordinarily adopted for its determination.

*Assay of lead.* Numerous methods have been suggested from time to time for the assay of lead both in the wet and dry way, but that involving fusion in contact with iron is generally practised, and is, at the same time, both easier and more reliable than other methods. It will therefore alone be described.

This process, available for the assay of all sulphides of lead, depends on the desulphurising action of iron at an elevated temperature. The iron may be applied by performing the operation in a wrought-iron crucible or dish, or by introducing a piece of hoop iron or nails into the mixture contained in an earthenware crucible. The first of these, the iron crucible, is generally preferred as giving results most closely in accord with the actual content of the sample operated upon.

The following assay-charges are recommended by Percy, No. 1. being specially for rich ores, comparatively free from vein-stuff, while No. II. is applicable for either rich or poorer ores:—

	I. Grains.	II. Grains.
Ore . . . . .	500	500
Carbonate of soda . . .	500	350
Borax . . . . .	—	150
Argol (bitartrate of potash) .	50	50

The ore, after being reduced to powder in an iron mortar, is dried at a moderate temperature, passed through a sieve of from 40 to 60 holes per linear inch, and the required sample weighed out and mixed with about three-fourths of the flux indicated above, the remainder being placed just behind it in the charging scoop; the borax, however, when used, is not mixed with the other constituents, but placed at the back of the scoop for charging, and behind the unmixed flux. Thus arranged the charge is introduced into the iron crucible, previously heated to dull redness, when it is at once re-introduced into the furnace. The temperature having been

gradually raised to full redness and any metallic globules &c. adhering to the walls of the crucible thrown into the molten mass, and all signs of effervescence having disappeared, the crucible is removed from the furnace in from 10 to 15 minutes after its introduction. After partial cooling the entire contents are poured into a hemispherical ingot mould, care being taken that no particles are left behind in the crucible. It only remains to detach the lead button from adhering slag by tapping on an anvil; clean with a brush and hot water or with dilute sulphuric acid, and weigh. Any sulphate or carbonate of lead present in the ore will be reduced by the argol added, but if the ore be a phosphate or carbonate, a modified assay-charge is adopted and earthenware crucibles are always employed. Percy gives the following as suitable, Nos. III. and IV. for a phosphate, and V. for a carbonate.

	III. Grains.	IV. Grains.	V. Grains.
Ore . . . . .	300	300	500
Carbonate of soda . . . . .	400	350	500
Charcoal powder . . . . .	20	—	—
Argol . . . . .	—	100	100
Borax . . . . .	30	30	30

*Assay of gold and silver.* These two metals are so constantly associated in nature and in the arts, and the principal stages in their assay by the dry way so closely resemble one another, that no inconvenience need result from treating of the assay of both together. Indeed, such an arrangement will render it possible to give a more connected account of the entire process.

In the case of ores, metallurgical products, 'sweep' containing gold and silver, &c. a preliminary operation is necessary in order to free the precious metals from associated vein-stuff, carbonaceous matter, &c., previous to the assay operation proper, but otherwise the dry assay of the precious metals by cupellation is the same for ores &c. as for bullion and other alloys containing gold and silver.

This preliminary treatment has for its object the collecting of all the precious metal present in the sample in a button of lead, a result which may be arrived at by either *scorification* or by *fusion*, often called the *pot method*. In cases where carbonaceous matter is present, as in the assay of 'sweep' or residues obtained from factories where the precious metals are manipulated, it is necessary to resort to a previous *roasting* or combustion. The following system is found convenient in the Royal Mint for making assays on 'sweep' containing a large proportion of graphite, the result of grinding up pots in which bullion has been melted, &c.

From the sample as received 2,400 grains are weighed, dried, and reweighed; the difference between these two weighings giving the moisture. Calling the second weight found W and the difference or weight of moisture M, we then have

$$W = (2400 - M) \text{ grains.}$$

The dried sample is ground in an iron mortar, passed through a sieve of 60 holes to the linear inch, and the metallic residue collected and cupelled separately. Calling the weight which passes through the sieve  $W_1$ , it is evident that  $\frac{W_1}{4}$  will be the proportion obtained from 600 grains of the initial sample.

This weight,  $\frac{W_1}{4}$ , is now roasted in a roasting dish (a, fig. 4), by heating to a red heat in an open muffle, whereby all combustible matter is removed. It is again weighed on cooling, and its weight,  $W_2$ , divided into three equal portions for scorification. Each of these portions,  $\frac{W_2}{3}$ , will thus correspond to 200 grains of the original sample.

For each scorification charge are taken 800 grains granulated lead and 50 to 100 grains borax (this somewhat increased portion as compared with that prescribed below being due to the intractability of the graphite); half the lead having been mixed with the above weight,  $\frac{W_2}{3}$ , and the borax, is placed in the scorifier (c, fig. 4), and covered with the remaining lead. The three scorifications are then proceeded with as explained below.

In preparing an ordinary sample for scorification, if an ore or other metallurgical product previously roasted, it is first weighed as received and after drying, and then reduced to powder and passed through a sieve having 80 holes to the linear inch, any metallic particles or 'metallics' left behind on the sieve being carefully collected and assayed separately. Percy recommends that the following proportions be taken for the charge:

Sifted ore . . . . .	50 grains.
Granulated lead . . . . .	500 to 1,000 grains.
Borax . . . . .	5 grains.

The ore being mixed with about half the lead in a scorifier, the remaining lead spread evenly over it, and the borax on the top, the scorifier is left in a muffle, with the door closed at first and then slightly opened, and heated above the temperature required for cupellation (v. page 210). On the conclusion of the operation, after about three-quarters of an hour's steady fusion, 3 or 4 grains of anthracite powder wrapped in paper are added in order to clear the mass of litharge of any particles of silver that may be entangled in it (by reducing a small quantity of the oxide to the metallic state), and the scorification will be complete as soon as quiescence is restored. The scorifier is at once removed and its contents poured into the mould (b, fig. 3). On cooling the slag is detached from the button of lead by a hammer, and this button is cupelled in the manner subsequently explained, to extract the precious metal it contains.

When the pot method is resorted to for collecting the silver, it is necessary to vary the proportions of the ingredients taken according to the composition of the ore operated upon. For ordinary qualities, containing only a small proportion of other metals, the following are recommended:—

Ore (according to richness) . . . . .	100 to 500 grains.
Red lead . . . . .	500 "
Charcoal powder . . . . .	20 to 25 "
Carbonate of soda (about) . . . . .	250 "
Borax . . . . .	250 "

The last two may require varying, an increase in one being accompanied by a corresponding decrease in the other.

After mixing the above (except a little of the borax) the charge is introduced into a crucible

by means of the scoop (c, fig. 3), and the remaining borax placed on the top. The temperature of the crucible is gradually raised, and in about a quarter of an hour it is removed from the furnace and its contents poured into a mould, as explained under 'scorification'; the subsequent operations are the same as there specified.

The method of assay of gold and silver by cupellation being the same, whether it be an alloy or a lead button, obtained by either of the above methods, it will be convenient to proceed at once to explain the several stages through which a bullion assay passes, as thereby repetition will be avoided and it will be obvious how much of the treatment described applies to the argentiferous or auriferous lead button.

*Cupellation assay of gold and silver.* If a current of air be allowed to pass over a bath of molten lead containing various other metals, the lead will be converted into its oxide—litharge—and this litharge will hold the oxides of such oxidisable metals as are present in solution. If, further, the containing vessel be porous, this solution will be absorbed as it is formed and, when the whole of the lead has been thus absorbed, there will only remain on the surface of the vessel such metals as are not oxidisable. Cupellation is the method by which this fact is taken advantage of for the removal of precious or nonoxidisable metals from others with which they may be associated.

In order to extract the gold or silver (or both together) from the lead buttons obtained as already explained by the pot and scorification methods, they are placed in 'cupels' (d, fig. 4) of convenient size, previously raised to a red heat in the muffle. The temperature is maintained and the draught regulated so as to gradually oxidise the lead in the manner above described; on the completion of this process, which is immediately preceded by the rapid passage of brilliant iridescent colours over the surface of the button, the furnace is closed to allow the button to set, and, when removed from the furnace, it only remains to detach adhering bone-ash by a brush and weigh. In cases in which gold exists in presence of silver the operation is, however, not yet complete, and the further treatment will depend on whether it is required to determine the silver present or not. In the first case a 'double parting,' and in the second a 'single parting' assay must be made in the manner explained below.

*Assay of gold bullion and alloys.* A piece of the metal to be examined is accurately adjusted to correspond in weight with a standard weight or 'assay pound.' This varies with different assayers from 5 grains to about 16, but  $\frac{1}{2}$  gram (or 7.716 grains) may be taken as a convenient unit. To this is added a piece of silver (free from gold) equal in weight to about  $2\frac{1}{2}$  times the gold estimated to be present in the alloy (which if not already known can be ascertained by a preliminary rough assay or by the touchstone, page 211) and the whole is wrapped in sheet lead, the weight of which depends mainly on the amount of copper to be removed, and varies from 8 to 32 times the weight of metal taken for assay. A number of these packets as they are formed are placed in numbered compartments in a divided tray which correspond

to the positions occupied by the cupels, already raised to a bright red heat in the muffle. Each packet having been transferred by a pair of long-nosed tongs (fig. 5) to its cupel, the muffle mouth

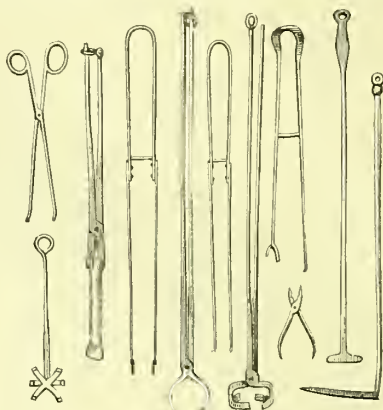


Fig. 5.

is nearly closed and the heat maintained. In from 10 to 20 minutes the iridescent band already referred to will be observed passing over the surface, and a few minutes later the muffle should be closed to allow the buttons to set, although some practised assayers prefer to save time by removing them while still molten. The buttons may now be considered to contain only gold, with about  $2\frac{1}{2}$  times its weight of silver, the lead having eliminated the copper and other oxidisable metals. The silver consists mainly of that added in making up the lead packets, but also includes such silver as *may* have been present in the gold. Indeed it is mainly this possibility of silver being present that renders it necessary to add the silver at all, for the gold would protect any small proportions of silver from the action of the nitric acid into which the assays are subsequently introduced, and so prevent its complete removal. The buttons (a, fig. 6) after being brushed to detach adhering bone-ash, are flattened, b (to about the size of a sixpence when a  $\frac{1}{2}$ -gram pound is taken), annealed and rolled in a small hand flattening mill to the thickness of a visiting card, c. After this 'fillet' has again been annealed, it is coiled into the form d (when it is known as a 'cornet'), between the thumb and first finger, in which form it is ready for treatment with nitric acid. If gold assays are only occasionally done, 'parting flasks,' b, fig. 4, suffice for this operation, but where large numbers are frequently made, the platinum boiling apparatus described below is strongly recommended; but in this case the assayer must have sufficient knowledge of the gold operated upon to be sure that none of the assays will break up in boiling, as such an accident would render all the others unreliable.

The first-named method is conducted as follows. The cornet is introduced into about 2 ounces of nitric acid (sp.gr. 1.2), previously raised to the boiling-point, and the boiling is continued for 10 minutes; the flask is nearly filled with hot distilled water, the liquid decanted,



and 2 ounces of stronger acid (sp.gr. 1.3) added and boiled for an additional 15 minutes. The flask having been filled twice with hot distilled water and decanted, is filled a third time and inverted, after placing a small porous crucible or 'annealing pot,' *e*, fig. 4, over its mouth. The pure gold thus falls gently into this pot, the flask being slowly raised allows water to fill it, and the flask itself can then be moved off horizontally while held vertical without disturbing

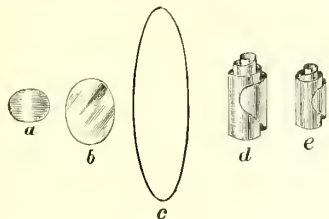


FIG. 6.

any fine particles in the pot. It only now remains to decant the liquid, dry and heat the pot to a dull redness, when the gold will cohere, *e*, fig. 6, and change in colour from red to the ordinary yellow tint, in which condition it is weighed.

The accompanying illustration (fig. 7) shows a pair of platinum boilers, as used in the Royal Mint. Each is 20 cm. in diameter and about 14 cm. deep, these dimensions depending on the size of the platinum tray to be introduced and

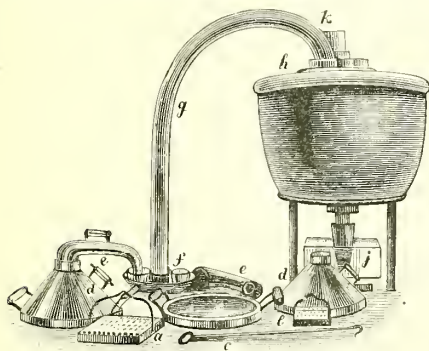


FIG. 7.

the amount of acid required. The tray *a* is perforated and contains 144 platinum cups or thimbles, also perforated, to allow of free circulation of the acid. A smaller tray, *b*, containing 36 cups, is also shown, for use when a small number only of assays require to be boiled, and it is used in conjunction with pans of corresponding size. The platinum hook, *c*, is for introducing or removing the tray. Heat is applied below by large Bunsen burners, and the hoods, *d, d*, rest in water troughs, as do also the condensing tubes, *c, c*. A portion of the acid vapour is condensed in a jar placed below the platinum connecting piece, *f*, while the remainder, passing up the earthenware tube, *g*, is received and condensed in a vessel contained in *h*, which is filled with water, and collected at *j*, any uncondensed fumes passing into the chimney

through a long vertical glass tube that rests in the opening *k*. Acids of the same strength as are used with flasks may be used in such pans, but the boiling should be more prolonged, and care is necessary that sufficient is present to ensure its not boiling to dryness. It is usual to wash the tray in hot distilled water before introducing it into the second pan. After removal from this latter the tray is washed and raised to a dull red heat in the muffle. On cooling the assays are ready for weighing, and it is usual to make two or more assays on chemically pure gold at the same time, and to apply the mean 'surcharge' or difference between their initial and final weighings as a correction to all the assays made at the time.

*Double parting assay.* The above is the method adopted for the determination of gold, but if it is required to ascertain also the amount of silver present, a slight modification becomes necessary. The sample is wrapped up as before, in lead foil, but no silver is added. The resulting button, having been brushed and weighed, is now again wrapped in lead with the necessary silver, and an ordinary parting assay made. The gold present is given by the weight of the cornet, and that of the silver by subtracting the weight of cornet from that of the button first obtained.

To determine small quantities of gold contained in silver, dissolve a weighed quantity in nitric acid (sp.gr. 1.2), collect, ignite, and weigh the resulting powder of gold.

*Assay by the touchstone.* This ancient method consists in comparing the colour of the streak produced by a sample of gold of unknown composition on a black surface with those from a series of known compositions, after all have been treated alike with nitric acid. Any abrading surface on which the acid is without action can be employed for this purpose.

*Assay of silver by the wet method.* When the proportion of silver present in an alloy is quite unknown, the cupellation method of assay already described is always adopted, but if the composition is known within certain narrow limits, as for example, when refined ingots or coin are in question, the volumetric method of Gay-Lussac has many advantages and is much employed. It depends on the fact that since silver is completely precipitated as chloride from its solution in nitric acid by the addition of hydrochloric acid or common salt, the quantity of pure silver present in solution can be ascertained by observing the bulk of a normal solution of either of these that is required for its complete precipitation. As an illustration of the method of procedure, let it be required to ascertain precisely the proportion of silver present in an alloy whose composition is known approximately to be 900 (that is, 900 parts in 1,000). Now take such a weight of the metal as to ensure there being rather more than 1 gram present in it. If *W* be the weight containing exactly 1 gram, of course  $W = \frac{1.000}{900} = 1.111$  gram alloy. The quantity required for assay will thus be, say, 1.115 gram, and this is dissolved in about  $\frac{1}{2}$  oz. of nitric acid (sp.gr. 1.2) with the aid of heat. A measured quantity of normal salt solution is now introduced from a pipette,

the form of which varies; that devised by Stas and containing 100 c.cm. is very convenient, and a pair, as used in the Royal Mint, adjusted to equal capacity, are shown in fig. 8. The liquid is first introduced into the pipette *d* through an indiarubber tube as shown at *a*, leading from a 20-gallon reservoir at an elevation of about 4 ft.; any solution that escapes at the upper end is received in the platinum

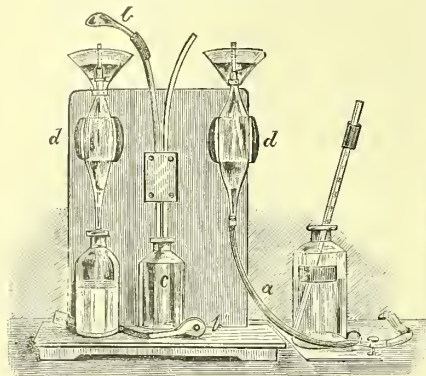


FIG. 8.

spoon-shaped tube *b*, the under side of which is shown by the detached tube *b'*, and by it led to the bottle *c*. When the pipette is full, the upper end is closed by the finger, the tube removed, and a bottle containing silver in solution placed underneath. The metal is immediately precipitated as a white chloride, which may be caused to agglomerate by a few minutes' shaking, either by hand or in a specially arranged shaking tray. If the normal solution is of the exact strength (and any deviation can be ascertained by making an assay concurrently on chemically pure silver), 1 gram of silver will have gone to form this chloride, and any excess will be retained in solution in the supernatant liquid; it only remains, therefore, to determine its amount. This is done by adding first 1 c.cm. of a decimal salt solution (each c.cm. of which will therefore precipitate 0.001 gram silver) and again shaking, after adding further c.cms. or not, as is judged necessary from an examination of the 'cloud' or superficial layer of chloride produced by that first added. This operation is continued until it is found that no further precipitate can be produced; the amount of silver present is then readily determined from the total amount of sodium chloride required for its precipitation. The observation of these delicate precipitates is much facilitated by standing the bottles on a dead black shelf in the window, with a ledge at the back of such a height that the light passes only through the upper portion of the liquid contained in them.

*Assay of silver by weighing the resulting chloride.* This method, ordinarily used at the Indian Mints, consists in taking a constant weight of the alloy (18.817 grains, *v. p.* 207) which is dissolved in nitric acid of sp.gr. 1.2 and diluted with water. An excess of hydrochloric acid is added to insure the precipitation of all silver present. After being two or three times

washed with distilled water and allowed to rest, the silver chloride is transferred to a cup, dried at a temperature not exceeding 170°C. and weighed while warm, the weights used giving the percentage of silver present in the alloy, without calculation, as explained at page 207.

W. C. R. A.

#### ASSAY OF FUEL *v.* FUEL.

**ASTATKI.** A Russian term, signifying 'dregs,' applied to the residue left in the distillation of Baku petroleum after the volatilisation of the kerosene, and now largely used as fuel in the Caspian region (*v.* PETROLEUM).

#### ASTERIA *v.* CORUNDUM.

**ASTRALINE.** Russian petroleum oil, used for burning (*v.* PETROLEUM).

**ASTRALITE.** A glass resembling aventurine, but containing crystals of a cupreous compound which by reflected light exhibit a dichroic iridescence of dark red and greenish blue. Made by fusing and allowing to cool slowly a mixture of 80 pts. silica, 120 lead oxide, 72 sodium carbonate, 18 borax, with either 24 pts. scale oxide of copper, and 1 pt. scale oxide of iron, or with 5 pts. lime, 26 copper oxide, and 2 iron oxide.

**ATACAMITE.** A native copper oxychloride, originally found in the desert of Atacama, Peru. It occurs in the mines of Schwartzberg, Saxony; abundantly at Algodon Bay; Bolivia; at Wallaroo, Yorke Peninsula, and at Burra Burra in Australia. It dissolves easily and completely in acids and ammonia.

#### Analyses:

Cu	Cl	CuO	OH <sub>2</sub>	SiO <sub>2</sub>
13.73	15.38	55.91	13.51	Insol. (from Wal-
				laroo Cloud, C. N. 34, 254).

CaCl <sub>2</sub>	CuO	OH <sub>2</sub>	SiO <sub>2</sub>
13.213	64.709	14.491	7.599 (Liversidge, C. J.
			[3] 40, 991).

(*v.* COPPER.)

**ATHAR or ATTAR.** Indian name for volatile oil of roses (*v.* ATTAR OF ROSES).

#### ATLAS DYNAMITE *v.* EXPLOSIVES.

#### ATLAS POWDER *v.* EXPLOSIVES.

#### ATLAS SCARLET *v.* AZO-COLOURING MATTERS.

**ATMOSPHERE.** The gaseous envelope surrounding any liquid or solid body; more particularly the gaseous envelope which surrounds the earth, and which is commonly known as air. The thickness of this aerial envelope is not known even approximately, but it is quite certain that it exceeds 45 miles measured from the earth's surface, which was the limit assigned to it by Wollaston. Secchi calculated that air exists even at a height of 200 kilometres above the earth's surface. The mass of the atmosphere forms, like the earth itself, an oblate spheroid, the polar axis of which is much shorter than the equatorial axis, the ratio of the two axes being, according to Laplace, as 2 to 3.

The pressure of the atmosphere at any particular spot may be measured in terms of the height of a column of mercury which it is capable of sustaining. It follows, from the law of Boyle, that the density of the air rapidly diminishes with the height. For air of constant temperature, its density, or, what comes to the same thing, the height of the mercurial column, should diminish in geometric progression whilst the distance from the earth increases in arithmetic progression. The pressure, even at the

same place, is continually varying, from a variety of causes, and hence the height of the barometer, as the mercurial column was first termed by Boyle, is practically never absolutely constant. The average height at any one spot at the sea-level is mainly dependent upon the great movements of air which result from the effect of the earth's motion upon the gaseous envelope, combined with variations in the density of the aerial mass due to solar action.

According to Regnault, 1 litre of dry air, free from carbonic acid and ammonia, measured at 0°C. and 0.76 m. pressure, at Paris (lat. 48° 50'), and at a height of 60 m. above the sea-level, weighs 1.293187 grams. Lasch found that 1 litre of pure air at standard temperature and pressure weighs at Berlin (lat. 52° 36') 1.293635 grams.

The Bureau Internat. des Poids et Mesures adopts for the weight of 1 litre of dry air, containing .01 p.c. carbonic acid, at the normal temperature  $t$ , and under the normal barometric pressure of 1 mm.,

$$Pti = \frac{1.293052}{1 + .00367} + \frac{1}{760}$$

on the assumption that .00367 is the expansion coefficient of air at constant pressure for a normal degree. For purposes of ordinary chemical calculation it may be assumed with sufficient accuracy that 1 gram of air measures at standard temperature and pressure 773 cc.

The total weight of the atmosphere is about 11 trillions of lbs., or about 5 trillion kilos., and the relative amounts of the chief constituents may be assumed to be —

	Trillions kgm.
Nitrogen . . . . .	4.041200
Oxygen . . . . .	1.218040
Carbonic acid . . . . .	.003156
	5.262396

Herschel calculated that, allowing for the space occupied by the land above the sea, the mass of the atmosphere is about  $\frac{1}{120000}$  part of that of the earth.

The unit of pressure adopted by engineers and others, and styled an *atmosphere*, is an amount equal to the average pressure of the atmosphere at the sea's level. In British measure an atmosphere is the pressure equivalent to 29.905 inches of mercury at 32°F. at London, and is about 14.73 lbs. on the sq. inch. In the metric system it is the pressure of 760 mm. (29.922 inches) at 0°C. at Paris, and is equal to 1.033 kilos. on a sq. centimetre. Hence the English 'atmosphere' is 0.99968 that of the metric system.

The specific heat of air at constant pressure is 0.2374 (Regnault). Its coefficient of thermal expansion between -30° and 200° is .003665 for 1°C.

Under a pressure of 200 atmospheres, and at the low temperature produced by the evaporation of liquid nitrous oxide, air may be liquefied.

Comparatively little of the sun's heat is absorbed in its direct passage through the air. According to Tyndall, a column of air 1 metre long absorbs 0.088 p.c. of the heat which passes through it. According to Violle, and also Lecher and Pernter, the amount is not greater than 0.070 p.c. This absorption is mainly due to

aqueous vapour, and, in a lower degree, to carbonic acid and suspended organic matter. The air mainly gets its heat by radiation from the earth, and hence, as a rule, it is hottest near the ground. The law of the decrement in temperature corresponding to height is not known; it is usually stated to be about 1° for every 195 metres, but the rate is liable to very great variations.

Air is not perfectly transparent. Its particles reflect and scatter light in sufficient quantity to obscure the light from the stars. The blue colour of the sky is due to the fact that the most refrangible rays are most widely scattered. In the higher regions of the atmosphere, where the amount of reflected light becomes less and less, owing to the increased density of the air, the sky appears to grow gradually darker. Brewster first proved that the blue light from the sky, as well as the white light from the clouds, was due to reflected light by the fact that it was polarised.

Suspended matter, dust, smoke, aqueous vapour in a state of partial precipitation, &c., greatly diminish the transparency of air. Wild gives the following numbers as representing the transparency coefficient of 1 metre of air:

Dry air (free from dust) . . . . .	0.99718
Air of a room (dry, but containing dust) . . . . .	0.99520
Air free from dust, but saturated with aqueous vapour . . . . .	0.99328

The refractive indices of dry air at standard temperature and pressure for the Fraunhofer lines A, B, C, D, E, F, G, H, are, according to Ketteler (P. 124-401), as follows:

$n_A = 1.00029286$	$n_E = 1.00029584$
$n_B = 1.00029345$	$n_F = 1.00029685$
$n_C = 1.00029383$	$n_G = 1.00029873$
$n_D = 1.00029470$	$n_H = 1.00030026$

The emission spectrum of air has been mapped by Huggins (T. 154, 139) and Angström (P. 94, 141), and the spectrum of lightning by Kundt (P. 135, 315), who has shown that forked lightning gives a line spectrum, whereas sheet lightning gives a band spectrum. The absorption spectrum of air was first mapped by Brewster and Gladstone, and has been further examined by Janssen and Cornu. Chappuis (C. R. 91, 988) has also studied this spectrum and comes to the conclusion that the blue colour of the sky is due to ozone; *v. also* Hartley (C. N. 42, 208).

Air, owing to the oxygen it contains, is a magnetic substance. The diurnal variation in magnetic declination has been ascribed to the varying magnetic potential of the oxygen due to alterations in temperature.

Air is a mixture of nitrogen, oxygen, aqueous vapour, carbon dioxide, with minute quantities of ozone, hydrogen peroxide, ammonia, nitrous and nitric acids, hydrocarbons, &c. That the air is not a chemical compound of its component gases is proved by the facts: (1) that these gases are not present in any constant ratio; (2) that air can be made by simply mixing its constituents in the proportion indicated by the analysis of air, without contraction or any thermal disturbance resulting; (3) that on treating air with water and expelling the dissolved air by boiling, the proportion of the oxygen to the nitrogen is found to be increased, and in amount corresponding with the law of partial pressures; (4) that



the constituents of the air can be mechanically separated by processes of diffusion; and (5) that the refractive power of the air is equal to the mean of the refractive powers of its constituents, whereas in compound gases the refractive power is either greater or less than the refractive power of the elements in a state of mixture.

The amount of oxygen in air may be ascertained by measuring the diminution in volume which a known bulk experiences when in contact with some substance capable of absorbing or combining with oxygen gas. Among the substances which may be conveniently used for this purpose are—

1. *Phosphorus*. A fragment of phosphorus on the end of a platinum or copper wire is exposed to a measured volume of air standing over water or mercury until no further decrease of volume is observed (Berthollet). Lindemann (Fr. 1879, 18, 158) employs thin sticks of phosphorus for the same purpose in the Orsat apparatus (*v. GAS ANALYSIS*). At temperature below 7° the oxidation of the phosphorus ceases.

2. *Pyrogallol in alkaline solution*. Chevreul, in 1820, first suggested the use of this reagent. The absorption is apt to be accompanied by the formation of notable quantities of carbon monoxide if the amount of oxygen is large or the alkaline solution very concentrated. According to Hempel (B. 20, 1865), the best proportions are 5 gr. pyrogallol dissolved in 15 c.c. water mixed with 120 gr. caustic potash dissolved in 80 cm. of water. Practically, no carbon monoxide is formed with this solution. The absorption is very rapid (Hempel, B. 18, 267 and 1,800).

3. *Metallic Copper*. A spiral of copper wire is heated to redness in dry air free from carbonic acid and of known tension until the whole of the oxygen has combined with the metal to form cupric oxide. The tension of the residual gas is then determined, whereby the amount of nitrogen is ascertained, and hence the amount of oxygen. An apparatus on this principle was suggested by Jolly (W. N. S. 6,538); it is seen in fig. 1.

The glass vessel A, of about 100 c.c. capacity, is exhausted by the mercurial pump, and is replenished with the air under investigation. This is then cooled to 0° by surrounding A with the metallic cylinder B, which is filled with melting ice. The tension of the confined air is measured by the height of mercury in the glass tubes g and d, which are connected together by caoutchouc tubing. The tube g is movable in the clamp f, the position of d being fixed with reference to A. By turning the three-way stop-cock b, A and d may be alone brought into connection, or both may be made to connect with the outer atmosphere. The cock is now so turned that A and d are alone in connection; the tube g is now raised until the level of the mercury in d just touches the point m, when the tension of the air is read off on the graduated scale behind g. The copper spiral in A is next heated to redness by an electric current, whereby the heated metal rapidly combines with the oxygen. The cylinder B is once more placed round A, the residual nitrogen cooled down to 0° by means of melting ice, and its tension measured by adjusting the level of the mercury to m,

and reading off the height of the mercury in g. If, for example, the pressure before abstracting the oxygen was 702.56 min., and after the abstraction was 555.70 min., then 1 volume of the

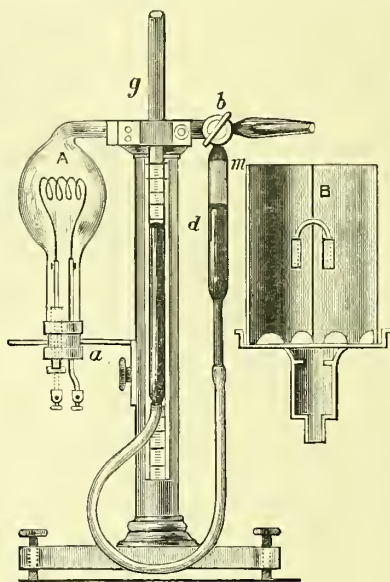


FIG. 1.

air would be reduced to =  $\frac{555.70}{702.56} = .79096$  vol., or expressed centesimally, the composition of the air would be

Nitrogen . . . . .	79.096
Oxygen . . . . .	20.904
	<hr/>
	100.000

Kreusler has shown that unless the air be carefully dried before being heated with the copper spiral the proportion of oxygen will be apparently too low.

Dumas and Boussingault (A. Ch. [3] 3,257), as far back as 1841, made use of the fact that heated metallic copper combines with oxygen in order to determine the gravimetric composition of air. Air deprived of moisture and carbonic acid was passed through a weighed tube containing metallic copper heated to redness whereby all the oxygen was absorbed, the nitrogen being collected in a vacuous glass globe also previously weighed. At the conclusion of the experiment the tube containing the metallic copper was again weighed; the increase in its weight gave the amount of absorbed oxygen together with the weight of the nitrogen which it also contained. The nitrogen was then removed by the air pump and the tube again weighed; the difference between the first and third weighing of the tube containing the copper gave the weight of absorbed oxygen and the weight of nitrogen was obtained by adding the difference between the second and third weighing of the tube to the increase in the weight of the glass globe. As the mean of a large number of experiments made by this method, the percentage

composition by weight of air free from water and carbonic acid was found to be:

Oxygen . . . . .	23.00
Nitrogen . . . . .	77.00
	100.00

4. *Explosion with hydrogen.* A measured volume of air is mixed with a known volume of hydrogen in excess and the mixture is exploded by the electric spark, when the oxygen combines with the hydrogen in the proportion of 1 vol. of the former to 2 of the latter to form water. One-third of the contraction resulting from the explosion represents therefore the amount of oxygen in the air under examination. This method, first suggested by Volta, was perfected by Bunsen. Modifications of the method have been made by Regnault and Reiset, Williamson and Russell, Frankland and Ward, and others. These methods are extremely accurate, and have afforded us all the exact knowledge we have respecting the variations in the amount of oxygen in atmospheric air. Thus Bunsen in a series of analyses made in the winter of 1846 found that the percentage amount varied from 20.97 to 20.84. Regnault made a large number of analyses of air collected from all parts of the world. In 100 analyses of air collected in Paris the minimum amount of oxygen was 20.913, the maximum 20.999. Air collected in various parts of Europe, from above the Atlantic Ocean, from the summits of the Andes and from the South Polar Sea, contained an amount of oxygen varying from 20.86 to 21 p.c. Many hundreds of analyses were made by Angus Smith of air collected in various towns in England and Scotland, and also of air collected in the country. The oxygen in London air varied from 20.857 to 20.93, less oxygen as a rule being found in the air of streets than in that of the parks and open spaces. A series of 30 analyses of Glasgow air showed variations from 20.887 in the closer parts to 20.929 in the more open spaces. Even wider extremes were found by Leeds in the air of New York, viz., from 20.821 to 21.029 p.c. According to E. W. Morley the diminished proportion of oxygen may be caused by the down-rush of air from the higher regions of the atmosphere which probably contain a less relative amount of oxygen. Regnault's experiments afford some evidence for the belief that the air of the tropics contains slightly less oxygen than that in northern latitudes (*v.* also Jolly, W. N. F. 61, 520). A similar conclusion has been drawn by Hempel (B. 20, 1864) from the analysis of a large number of analyses of air collected simultaneously at Tromsø, Dresden, and Paris. The mean results were:

	Oxygen
Tromsø . . . . .	20.92
Dresden . . . . .	20.90
Paris . . . . .	20.89

From the results of 203 analyses of air collected at five different spots and analysed by three independent methods, it follows that the most probable mean percentage amount of oxygen was 20.93. The maximum 21.00 was observed at Tromsø on April 22, 1886, the minimum 20.86 at Paris on April 26, 1886 (Hempel, B. 20, 1864; Kreusler, B. 20, 991).

Ozone is always present in minute quantity in normal air. Air over marshes contains little

or no ozone. No ozone can be detected in the air of large towns or in inhabited houses. Atmospheric ozone is probably formed by the action of electricity on air and on the water contained in it, and by the evaporation of water. No accurate quantitative method is known for the estimation of ozone; all the information we at present possess has been obtained by the use of so-called ozone-papers. Of these the best known is Schönbein's, which is based on the fact that ozone liberates iodine from potassium iodide and thereby renders starch blue. To prepare them unsized paper is immersed in a solution of 15 parts starch and 1 part potassium iodide in 200 parts of water and dried in the dark. To make a determination of ozone the paper is freely exposed to the air for some hours and moistened with water, and the depth of tint produced compared with a standard scale of colour. The method has no pretensions to scientific accuracy. Houzeau (A. Ch. 4, 27, 5) determines the relative amount of ozone by exposing red litmus paper previously dipped in 1 p.c. sol. of potassium iodide and dried, to the action of the air. The ozone liberates iodine and the free alkali turns the paper blue. Thallium salts are turned brown by the action of ozone, and hence papers soaked in solution of these salts have been used for the recognition of ozone. Paper soaked in a very dilute solution of neutral gold chloride is turned a deep violet colour by ozone (Böttger, C. C. 1880, 719).

Attempts have been made to estimate ozone by aspirating large volumes of air through dilute solutions of hydriodic acid and determining the amount of the liberated iodine by iodometric analysis. Also by leading the air through a mixed solution of potassium arsenite and potassium iodide whereby the liberated iodine converts the arsenite to arsenate. The liquid through which the air had passed was then mixed with a few drops of ammonium carbonate solution and starch paste, and a standard solution of iodine (1:1,000) added until the blue colour was permanent. A precisely similar experiment was made on equal amounts of distilled water, iodine, arsenite &c. used, and from the difference in the amount of iodine solution needed the amount of oxidised arsenite and hence the quantity of ozone was determined.

It appears that the amount of ozone varies with the seasons: it is greatest in spring, becomes gradually less during summer and autumn, and is least in winter. Ozone is more frequently observed on rainy days than in fine weather: thunderstorms, gales, and hurricanes are frequently accompanied by relatively strong manifestations of it.

It is highly probable that many so-called ozone manifestations are due to *hydrogen peroxide*, the existence of which in the air was first demonstrated by Meissner in 1863. Unfortunately there is no ready mode of discriminating between ozone and hydrogen peroxide. It is probable that the amount of hydrogen peroxide in the air is as a rule greater than that of ozone. Schöne found from observations made at Moscow that it was invariably present in rain, dew, and snow, and was less in winter than in summer; and more in southerly winds than in those from the north. The amounts in all cases were, how-

ever, very minute, the maximum being 1·4 c.c., and the mean 0·38 c.c. hydrogen peroxide vapour in 1,000 cc. air.

The quantity of *aqueous vapour* in the air varies with the temperature: thus 1 cm. of air when saturated with water contains

At -10°	2·284	grams	At +20°	17·157	grams
0°	4·871	"	25°	22·843	"
+ 5°	6·795	"	30°	30·095	"
10°	9·362	"	35°	39·252	"
15°	12·746	"			

The most accurate method of determining the amount of aqueous vapour in the air consists in aspirating a given volume of the air through weighed tubes filled with some hygroscopic substance, such as calcium chloride or phosphoric oxide or pumice soaked in oil of vitriol and re-weighing the tubes, when the increase of weight gives the quantity of moisture present.

Usually, however, the humidity of the air is estimated by means of hygrometers, the best-known form of which is the psychrometer or wet and dry bulb thermometer of August. The *absolute humidity* of the air is the weight of aqueous vapour contained in 1 cm. The *relative humidity* denotes the relation between the weight actually present and that which could be theoretically present if the air were saturated; it is usually expressed in per cent. of the maximum humidity. The air is seldom absolutely saturated with aqueous vapour, although in our moist climate saturation is occasionally very nearly attained. With us the most humid month is January, and the driest is May.

The presence of *carbonic acid* in the atmosphere was first indicated by Macbride in 1764. The quantity in normal air is about ·03 p.c.; in that of large towns it is slightly greater. Angus Smith gives the following summary of results obtained in London in 1864 and 1869 (Air and Rain, 53-58):

Over River Thames	. 8 expts.	·0343 p.c.
In the Park	. . . 5 "	·0301 "
In the streets	. . . 10 "	·0380 "
Metropolitan Railway—(mean of 6 expts. on air taken from Nov. 12 to Nov. 15).	Oxygen = 20·70 p.c.	0·1452

Any circumstance which interferes with the ready diffusion of the products of respiration and the combustion of fuel will of course tend to increase the relative amount of carbonic acid in the air of a town: hence during fogs the amount may be as great as 0·1 p.c.

The amount of carbonic acid in the air of the country at night is usually greater than in the day, as the following comparison shows:

*Air in the day-time.*

Observer	Year	Place	No. of expts.	Amount
Fr. Schulze	1861-71	Rostock	1034	·0299 p.c.
T. Reiset	1873-80	Ecorchebœuf	104	·0290 "
G. F. Armstrong	1879	Grasmere	27	·0296 "
Müntz & Aubin	1881	Vincennes	35	·0284 "
A. Levy	1877-83	Montsouris	2500	·0299 "
			3700	·0299 Mean

*Air in the night-time.*

T. Reiset	1873-80	Ecorchebœuf	72	·0304 p.c.
G. F. Armstrong	1879	Grasmere	29	·0330 "
			101	·0317 Mean

These differences are mainly due to the exhalation of carbonic acid from plants at night, and, to a smaller extent, to the absence of any decomposition of the gas by the action of sunlight. Over the sea this diurnal variation is not perceived, as the following results indicate:

*Carbonic acid in sea-air.*

Observer	Place	Year	Time	No. of expts.	Amount
T. E. Thorpe	Irish Channel and Atlantic Ocean	1865-6	Day	24	·0301 p.c.
			Night	20	·0299 "
				44	·0300

Comparatively few observations of the amount of carbonic acid in other parts of the earth than Europe have been made. The following may be cited:

*Carbonic acid in the air of tropical countries.*

T. E. Thorpe	S. America	1866	31	·0328 p.c.
Müntz & Aubin	S. & Central America	1882	40	·0278 "
			71	·0303

The pressure exerted by the carbonic acid in air is so small that its amount is not perceptibly diminished by rain. The amount also is not sensibly altered in the higher regions of the atmosphere.

Of the several methods which have been proposed for the estimation of atmospheric carbonic acid the most generally convenient is that of Pettenkofer. It consists in exposing a known volume (say 50 c.c.) of dilute baryta water of known strength to a measured quantity of air (4 to 6 litres) contained in a well-closed flask. In about 5 or 6 hours the absorption of the carbonic acid will be complete, provided that the sides of the flask have been moistened from time to time by the baryta solution. The baryta solution is then decanted and allowed to stand in a small stoppered bottle until the barium carbonate has settled, when aliquot portions (say 20 c.c.) of the clear solution are withdrawn and the amount of the baryta still in solution determined by titration with a standard solution of sulphuric or hydrochloric acid, of which 1 c.c. = 1 mgm. CO<sub>2</sub>, phenol thaleïn being used as indicator (*v. ACIDIMETRY*). The difference in the volume of acid needed for the neutralisation of the baryta before and after exposure to the confined volume of air gives the number of milligrams of carbonic acid contained in the air. Blochmann (A. 237, 72) has described a modification of the apparatus which allows of the titration being effected without exposure to the air of the laboratory.

For other methods *v. Haldane and Pembrey*, P. 1889; *Cl. Winkler*, Chem. Unter. der Industrie, Freiberg 1877; *Reiset*, C. S. 90, 1, 141; *Müntz and Aubin*, C. R. 92, 247.

For Angus Smith's minimetric method, *v. Air and Rain* (compare *Lunge*, D. P. J. 231, 331).

On the influence of the sea upon the amount of atmospheric carbonic acid, *v. Levy* (A. Ch. [3] 34, 5); *Thorpe*, C. J. 1867; *Schloesing*, C. R. 93, 1, 410; *Lawes*, P. M. (5) 11, 206.



Minute quantities of ammonia and nitrous and nitric acids are also present in the air. Although many of the published observations are probably inaccurate owing to the imperfection of the methods employed, it appears to be proved that the amount of ammonia, which exists mainly as carbonate, is subject to very great variations. By aspirating from 10 to 20 litres of air through Nessler's solution (an alkaline solution of potassium-mercury iodide) and comparing the depth of colour with that produced by a standard solution of an ammonium salt, H. T. Brown (P. 18, 286) found that the air of Burton-on-Trent during September, October, and November, 1869, taken 2 metres from the ground, contained from '4059 to '8732 parts ( $\text{NH}_4\text{CO}_3$ ) in 100,000 parts of air, whereas that of the country taken during December and February contained from '5102 to '6085 parts. The direction of the wind had apparently no influence on the amount; heavy rain seemed to diminish it, but the air was restored to its normal condition in a few hours. Truchot found from 0.93 to 2.79 mgm. per cubic metre in the air of Auvergne, the minimum being found in clear weather and the maximum during fogs (C. R. 77, 1,059). Müntz and Aubin from observations on rain water found that the upper strata of air contain much less ammonia than air near the ground. Levy (C. R. 91, 94) found that the rain water and snow of Paris contain in mean 1.17 mgm. of ammoniacal nitrogen per litre of water. The amount of ammonia in this meteoric water is least in winter and greatest during the warmer periods of the year. Lawes and Gilbert found that 1,000,000 pts. of rain water collected in the country contained from 0.927 to 1.142 pts. of ammonia. Rain water collected in towns always contains large quantities of ammonia. Thus Angus Smith found that rain water collected in the sparsely populated districts in Scotland contained 0.53 pts. per million, whereas the rain water of London contained 3.45, that of Liverpool 5.38, that of Manchester 6.47, and that of Glasgow 9.1 per million. The increased amount in the towns is doubtless due to the influence of animal life and to the constant presence in greater proportion than in the country of readily decomposable nitrogenous organic matter in the air.

The quantities of nitrous and nitric acids in the air are even smaller than that of ammonia. Angus Smith (Air and Rain, 287) has given the following results showing the amount contained in a million pts. of rain water:

Scotland, inland country places	0.305
Ireland " " "	0.370
Scotland, country places	0.424
" towns	1.164
England, inland country places	0.749
" towns	0.863

Occasionally, and more especially in the air of towns, minute quantities of hydrocarbons, sulphuretted hydrogen, carbonic oxide, sulphurous acid, common salt, alkaline sulphates are met with. Boracic acid and sal ammoniac have been observed in air in the neighbourhood of active volcanoes.

Organic matter in greater or less quantity is always present in the air. Much of this is

nitrogenous and apparently readily susceptible to putrefaction, giving rise to products which are alternately transformed into ammonia, nitrous and nitric acids. This form of organic matter reduces silver nitrate and potassium permanganate solutions. A portion of the organic matter consists of micro-organisms which are rapidly deposited in the absence of strong aerial currents. Hesse quantitatively estimates the relative proportions of micro-organisms contained in air by aspirating a given volume of the air through glass tubes coated internally with gelatine peptone which is then kept at a temperature of about  $25^\circ$  for some days, when the various monad bacilli and micrococci which are arrested and which are capable of growing in the gelatine-peptone are recognised by the colonies which they form. By means of this method Dr. Percy F. Frankland has made a number of estimations of the micro-organisms contained in the air of towns and in the country and in inhabited buildings. By simultaneously exposing small circular glass dishes partially filled with the nutrient gelatine to the action of the air, a rough estimate was obtained not only of the number of micro-organisms in a given volume of the air, but also of the number which fell during a given time on a definite horizontal area. As the mean of a series of observations made on the roof of the South Kensington Museum between January and June, 1886, it was found that there were 35 organisms in 10 litres of air, whilst 279 was the average number which fell on 1 sq. ft. in 1 minute. Similar experiments made near Reigate and in the vicinity of Norwich showed an average of 14 organisms in 10 litres of air, while 79 fell per sq. ft. per minute. Experiments made in Kensington Gardens, Hyde Park, and on Primrose Hill gave an average of 24 organisms in 10 litres, and a deposition of 85 per sq. ft. per minute. At St. Paul's Cathedral 56 organisms were found at the base, 29 in the Stone Gallery and 11 in the Golden Gallery in 10 litres of air. At Norwich Cathedral 18 at the base, 9 at a height of 180 ft. and 7 at 300 ft. In inhabited buildings great variations were observed; as a rule the number of micro-organisms was less than was found in the open air when the air of the room was undisturbed, but rose rapidly when the air was set in motion by draughts or by the presence of many people (P. F. Frankland, Pr. 40, 509).

Experiments made at the Montsouris Observatory have shown that far fewer organisms are present in the air during winter than during spring and summer. The number also seems to be greatly increased after rain. Whilst in the warm months the number of spores in 1 litre of air was 28, after heavy rain it rose to 95 and 120.

Atmospheric dust is made up of both inorganic and organic matter. Tissandier found that 1 cm. of the air of Paris contained on the average 7.5 mgms. of dust; after a period of dry weather (8 days) 23.0 mgms., and after heavy rain only 6.0 mgms. It consisted of from 27 to 34 p.c. volatile matter and from 66 to 75 p.c. mineral matter, viz. sulphates and chlorides of the alkalis and alkaline earths, oxides of iron, earthy carbonates and phosphates, &c.

## ATOMIC WEIGHTS AND SYMBOLS OF THE ELEMENTS

Aluminium . . . . .	Al	27.04
Antimony (Stibium) . . . .	Sb	119.6
Arsenic . . . . .	As	74.9
Barium . . . . .	Ba	136.86
Beryllium . . . . .	Be	9.08
Bismuth . . . . .	Bi	207.5
Boron . . . . .	B	10.9
Bromine . . . . .	Br	79.76
Cadmium . . . . .	Cd	111.7
Cesium . . . . .	Cs	132.7
Calcium . . . . .	Ca	39.91
Carbon . . . . .	C	11.97
Cerium . . . . .	Ce	141.2
Chlorine . . . . .	Cl	35.37
Chromium . . . . .	Cr	52.45
Cobalt . . . . .	Co	58.6
Copper (Cuprum) . . . . .	Cu	63.18
Decipium . . . . .	Dp	?
Didymium . . . . .	D	145.0
Erbium . . . . .	E	166
Fluorine . . . . .	F	19.06
Germanium . . . . .	?	?
Gold (Aurum) . . . . .	Au	196.8
Hydrogen . . . . .	H	1.00
Indium . . . . .	In	113.4
Iodine . . . . .	I	126.54
Iridium . . . . .	Ir	192.5
Iron (Ferrum) . . . . .	Fe	55.88
Lanthanum . . . . .	La	138.5
Lead (Plumbum) . . . . .	Pb	206.39
Lithium . . . . .	Li	7.01
Magnesium . . . . .	Mg	23.94
Manganese . . . . .	Mn	54.8
Mercury (Hydrargyrum) . . .	Hg	199.8
Molybdenum . . . . .	Mo	95.9
Mosandrium . . . . .	Ms	?
Nickel . . . . .	Ni	58.6
Niobium . . . . .	Nb	93.7
Nitrogen . . . . .	N	14.01
Norwegium . . . . .	Ng	?
Osmium . . . . .	Os	195
Oxygen . . . . .	O	15.96
Palladium . . . . .	Pd	106.2
Phosphorus . . . . .	P	30.96
Platinum . . . . .	Pt	194.3
Potassium (Kalium) . . . . .	K	39.03
Rhodium . . . . .	Rh	104.1
Rubidium . . . . .	Rb	85.2
Ruthenium . . . . .	Ru	103.5
Samarium (Yb ?) . . . . .	Sa	?
Scandium . . . . .	Sc	43.97
Selenium . . . . .	Se	78.87
Silicon . . . . .	Si	28.3
Silver (Argentum) . . . . .	Ag	107.66
Sodium (Natrium) . . . . .	Na	22.995
Strontium . . . . .	Sr	87.3
Sulphur . . . . .	S	31.98
Tantalum . . . . .	Ta	182
Tellurium . . . . .	Te	126.3
Terbium . . . . .	Tb	?
Thallium . . . . .	Tl	203.7
Thorium . . . . .	Th	231.96
Thulium . . . . .	Tm	?
Tin (Stannum) . . . . .	Sn	117.35
Titanium . . . . .	Ti	48.0
Tungsten (Wolfram) . . . . .	W	183.6
Uranium . . . . .	U	239.8
Vanadium . . . . .	V	51.1

## ATOMIC WEIGHTS AND SYMBOLS—continued.

Y <sub>a</sub> and Y <sub>β</sub> . . . . .	*	?
Yttrium . . . . .	Y	89.6
Zinc . . . . .	Zn	64.88
Zirconium . . . . .	Zr	90.4

**ATOPIITE.** A mineral containing 72.61 p.c. Sb<sub>2</sub>O<sub>3</sub>, 17.85 CaO, 2.79 FeO, 11.53 MnO, 0.86 K<sub>2</sub>O, and 4.40 Na<sub>2</sub>O (Nordenskiöld, J. 31, 1, 275).

**ATRAMENTUM STONE.** (*Atramentumstein*, Ger.) A product of the partial oxidation of iron pyrites, consisting of a mixture of ferrous and ferric sulphates with free ferric oxide. Used in the manufacture of ink.

**ATROPINE** v. VEGETO-ALKALOIDS.

**ATTAR, OTTAR** or **OTTO** of **ROSES**, is the volatile oil obtained by distilling roses, or, in some districts, by simple maceration of those flowers. It is a mixture of a fluid nitrogenous essential oil, and a crystallisable, non-nitrogenous stearoptene, which latter is most abundant in samples from colder regions, which consequently congeal more readily.

Attar of roses is made in Hindostan, Persia, and the Balkans; from which last-named district the largest part of the European supply is derived.

The trade in the article is nearly all centralised at Kezanlik. The method of producing it is as follows:—10 kilos of dry roses of the strongly scented Muscat variety are placed in a still of peculiar shape together with 70 kilos of water, and the distillate collected by a simple condenser; this gives about 20 kilos of rose-water, which is redistilled and the drops of otto of roses floating upon the surface of the product are collected. Pure Turkish (Roumelian and Bulgarian) otto of roses congeals at 14°C. Italian otto of roses congeals at 16.5°C. A sample of otto of roses produced from English-grown roses at Mitcham melted at 21°C.

Small quantities are produced in the south of France and the Italian borders. In 1887 an attempt was made to produce it in Germany, when about 25 acres were laid out for the cultivation of roses near Leipzig, and yielded in the first year 2 kilos of oil and 3,000 kilos of rose-water. 1,000 kilos. of rose-leaves is required to yield 1 kilo. of oil. It was said that the German oil had a superior perfume to that imported from Kezanlik, which costs about 700 marks per kilo.

Attar of roses is frequently adulterated with the otto of *Geranium rosa*, rosewood (*Convolvulus scoparius*) and sandalwood oils.

**AURAMINE** *Imidotetramethyldiparamido-diphenylmethane* C<sub>17</sub>H<sub>21</sub>N<sub>3</sub>.HCl + H<sub>2</sub>O or NMe<sub>2</sub>.C<sub>6</sub>H<sub>4</sub>.C(NH).C<sub>6</sub>H<sub>4</sub>.NMe<sub>2</sub>.HCl + H<sub>2</sub>O.

Auramine, the first member of a series of yellow, orange-yellow or brown dyes, is the hydrochloride of a colourless base obtained by the action of ammonia on tetramethyldiamido-benzophenone, and comes into the market either in the nearly pure form as *Auramine O*, or mixed with dextrin as *Auramine I.* and *II.* (Graebe, B. 20, 3261). Fehrmann (B. 20, 2847) proposed to restrict the name auramine to the colourless base, but such a change would inevitably lead to confusion, and Graebe (*loc.*) has

consequently adopted the name *auramine-base* for the base itself, using the term auramine in its usual signification.

*Preparation.*—(1) When tetramethyldiamidobenzophenone, dissolved in some indifferent solvent, such as chloroform, carbon bisulphide, hydrocarbons, &c., is treated with half its weight of phosphorus trichloride or oxychloride, a solution of the chlorinated compound is obtained (B. A. S. F., Germ. Pat. 27,789, Dec. 18, 1883), which on treatment in the cold with a considerable excess of concentrated ammonia at once becomes yellow, and after some time deposits auramine in a crystalline form. After filtration the auramine is freed from unattacked ketone by solution in dilute acetic acid, and then precipitated by the addition of soda or common salt and zinc chloride.

(2) Auramine can be prepared more economically by heating tetramethyldiamidobenzophenone with suitable ammonium salts, such as the chloride, acetate, tartrate, thiocyanate, &c., in the presence of zinc chloride. For this purpose an intimate mixture of equal weights of tetramethyldiamidobenzophenone, ammonium chloride and zinc chloride is introduced into an enamelled pot heated at 200° in either an air or an oil bath, and vigorously stirred from time to time. The mass gradually melts, becoming deep yellow in colour, and the reaction, which requires 4 to 5 hours for its completion at a temperature of 150–160°, is ended when a test specimen of the melt dissolves almost completely in water. The melt is allowed to cool, and, after powdering, is treated with slightly acidified cold water, to remove as much as possible of the excess of ammonium and zinc chlorides, and then exhausted with water at 60–70° to extract the auramine from any unattacked ketone. Auramine is finally precipitated from this solution by addition of common salt, and further purified by recrystallisation from warm water (B. A. S. F., Germ. Pat. 29,060, March 11, 1884). Acetamide may be employed instead of ammonium salts (B. A. S. F., Germ. Pat. 38,433, June 3, 1886), or the dye may be obtained by heating aniline hydrochloride with zinc chloride and carbamide, phenylcarbamide, diphenylcarbamide or carbanil (Ewer and Pick, Germ. Pat. 31,936, May 9, 1884), but these alternative methods have no practical importance.

*Properties.*—Auramine crystallises from water in yellow scales, which seem to consist of six-sided tables, and from alcohol in golden-yellow scales, melts at 267° (Graebe), carbonises at 265–280° without previous fusion (Fehrmann), and is sparingly soluble in cold, but readily soluble in hot water; the temperature of the aqueous solution, however, must not exceed 60–70°, otherwise decomposition ensues with the formation of ammonia and tetramethyldiamidobenzophenone. On treatment with mineral acids the aqueous solution undergoes a similar decomposition either slowly in the cold or very rapidly on heating. Spectroscopically, auramine behaves like most yellow dyes; a hot concentrated aqueous solution, however, shows two bands, one in the red and one in the green, which become broader on dilution and finally coalesce, forming a bright broad band extending from the

middle of the red to the commencement of the green (Graebe). On treatment in the cold with ammonia, auramine (crystallised from alcohol) is converted into the colourless base  $C_{17}H_{21}N_3$ , which melts at 136° and is characterised by yielding with acids intensely yellow, and for the most part crystalline salts, which dissolve in water and alcohol without fluorescence. Alkaline reducing agents, such as sodium amalgam, slowly decolourise the alcoholic solution of auramine forming *leukauramine*  $C_{17}H_{25}N_3$ , a colourless crystalline reduction compound melting at 135°, which dissolves in acetic acid with an intense blue colour owing to its decomposition into ammonia and tetramethyldiamidobenzhydrol.

Auramine dyes wool and silk direct, producing colours which are pure yellow and fairly fast to light and soap. Cotton, for which the dye is chiefly used, requires to be first mordanted with tannin and tartar emetic, and on this account auramine is useful for producing compound shades with other basic colouring matters, such as saffranine, benzaldehyde-green, &c., which are fixed by the same mordant. For further information *v.* Köchlin, W. J. 1884, 1139.

*Auramines.* In addition to auramine, substituted auramines have also been prepared. *Metaxylylauramine*, for example, can be obtained by heating an intimate mixture of 10 kilos. of tetramethyldiamidobenzophenone and 23 kilos. of metaxylylidine hydrochloride for about 4 hours at 200° in an enamelled vessel provided with a mechanical stirrer. Fusion takes place slowly and the mass becomes reddish yellow in colour, assuming finally a greenish metallic lustre towards the close of the reaction, which is complete when a test specimen of the melt is almost entirely soluble in water. The cooled mass is extracted with hot water and the dye precipitated in the form of orange yellow flocks by addition of sodium nitrate to the filtered solution.

The hydrochlorides of other bases can be employed instead of metaxylylidine hydrochloride, and dyes are obtained which are readily fixed by silk and wool, and also by cotton after mordanting with tannin. The shades produced on cotton are, however, distinctly reddish or brownish-yellow compared with the pure yellow produced by auramine itself; for example, the auramines from orthotoluidine, metaxylylidine and eumidine hydrochlorides dye cotton golden-yellow; those from aniline and paratoluidine dye orange-red, that from metaphenylenediamine dyes orange-brown, and those from  $\alpha$ - and  $\beta$ -naphthylamine dye brownish-yellow shades (B. A. S. F., Germ. Pat. 29,060; Fehrmann, B. 20, 2852).

**AURANTIA** (*Kaisergelb*) is the name given commercially to the ammonium salt of hexanitrodiphenylamine.

*Hexanitrodiphenylamine*  $NH[C_6H_4(NO_2)_3]_2$  is obtained by treating diphenylamine or methyldiphenylamine with nitric acid, and after the first vigorous action has subsided, heating to complete the reaction. The product is then extracted with water to remove any resin or picric acid associated with it, and finally crystallised from acetic acid.



It crystallises in bright yellow prisms, melts at  $238^{\circ}$  with decomposition but can be sublimed in yellow needles by careful heating, and is almost insoluble in water, more soluble in alcohol, and easily soluble in ether. It readily yields salts, and the *ammonium* salt (aurantia) crystallises in lustrous brown-red needles, although commercially it is obtained as a brick-red powder which dissolves in water and dyes silk and wool a beautiful orange colour (Gnehm, B. 7, 1399; 9, 1245; cf. Townsend, B. 7, 1249; Mertens, B. 11, 845). Aurantia is now used chiefly as a dye for leather (W. J. 1877, 1002). Like hexanitrodiphenylamine it is very explosive, but any danger may be avoided by moistening it with glycerine (W. J. 1876, 996). According to Gnehm (B. 9, 1246, 1557) and Bayer & Co. (W. J. 1877, 879), aurantia produces skin eruptions; Martius, however, contends that this effect is due to idiosyncrasy and quotes the opinions of Salkowski and Ziureck in support of his statement (B. 9, 1247), and the question appears to have received a solution in this sense in Germany, since the ministerial order of November 8, 1877, prohibiting its manufacture, was cancelled in June 1880 (W. J. 1880, 785).

#### AURANTINE v. ABIETENE.

**AUREOSIN.** An orange colouring matter of unknown constitution obtained by the action of hypochlorous acid on fluorescein. Discovered by Willm, Bouchardat and Girard, in 1876. By the action of nitric acid yields *Rubeosin*, a yellowish-brown powder soluble in alcohol and in caustic soda with a green fluorescence. Both dyes are no longer made.

#### AURINE and ROSOLIC ACID.

**History.**—Rosolic acid was first discovered and its tinctorial properties described by Runge (P. 31, 65), who obtained it from coal-tar oil by dissolving the residue from the distillation of phenol in alcohol, adding milk of lime, filtering off the brown precipitate of calcium brunolate and precipitating the red solution of calcium rosolate with acetic acid. Later, Tschelnitz (J. pr. 71, 416) and Müller (C. S. Q. J. 11, 1) found that the yield was greater if the product after addition of the lime was heated in the air for some time, whilst Smith (J. 1857, 448) and Jourdin (J. 1861, 943) showed that crude phenol was converted into rosolic acid by heating with soda and manganese dioxide or mercuric oxide. Kolbe and Schmitt (A. 119, 169) and, simultaneously, Persoz (Fr. Pat. 54,910, July 21, 1861) obtained it by heating phenol and oxalic acid with sulphuric acid, and this method was adopted for preparing the acid on the large scale by Wurtz (Schmidt, D. P. J., 166, 318) who termed it (yellow) coralline (known commercially as aurine in England), and by Guinon, Marnas and Bonnet (D. P. J. 167, 390), who converted it into pæonine or red coralline by digestion with aqueous ammonia at  $150^{\circ}$ . The reaction was further investigated by Fresenius (J. pr. [2] 5, 184), by Prud'homme (Bl. [2] 19, 359), and by Comaille (C. R. 77, 678), the last of whom found that the proportion of oxalic acid used was too large. By diazotising rosaniline Caro and Wanklyn (C. N. 14, 37; Pr. 15, 210) obtained rosolic acid  $C_{20}H_{16}O_3$  which, however, was not identical with the product from phenol.

Caro (P. M. [4] 32, 126), moreover, showed that the formation of rosolic acid from phenol is dependent on the presence of cresol or of some simple (methane) derivative of the fatty series of organic compounds (compare Guareschi, B. 5, 1055; Zulkowsky, A. 194, 122). The nature and composition of the products obtained in Kolbe and Schmitt's reaction were not, however, accurately known until 1878, when the researches of Dale and Schorlemmer (A. 166, 279; 196, 75), Caro and Graebe (A. 179, 184; B. 11, 1116, 1348), E. and O. Fischer (B. 11, 473) and Zulkowsky (A. 194, 122; 202, 179) conclusively proved that the action of oxidising agents on a mixture of phenol and cresol, or of oxalic acid on phenol results in the formation of a mixture of red colouring matters (coralline) containing two well-characterised substances termed aurine  $C_{10}H_8O_3$  and methylaurine  $C_{20}H_{16}O_3$ . Aurine is the lower homologue of Caro and Wanklyn's rosolic acid, and is sometimes known as pararosolic acid since it can be obtained by diazotising pararosaniline (E. and O. Fischer, A. 194, 268).

**Coralline.** This name is applied to the red colouring matter obtained by heating phenol and oxalic acid with sulphuric acid (*v. Aurine*) and, according to Zulkowsky (*l.c.*), is a mixture of pseudorosolic acid or corallinephthalin (70 p.c.), to which it owes its resinous consistency, with aurine and methylaurine. Methods for the isolation of these bodies are given under aurine (*q. v.*)

**Properties.**—It is a brittle resinous substance with a green metallic lustre, and yields a red powder. It is employed as a dye for silk and wool, and is also used for printing on cotton, silk, and wool (compare W. J. 1872, 707). For dyeing silk or wool, Schröder (D. P. J. 204, 397) dissolves coralline in alcohol, adds some soda ley, pours the solution into much water and renders it feebly acid with tartaric acid. In printing with coralline, it is necessary to adopt means to neutralise any acids with which it may come in contact during the process, otherwise a yellow instead of a turkey-red colour is the result. Kielmeyer recommends magnesia for this purpose in wool and cotton printing, and gives the following proportions:—80 grams of coralline,  $\frac{1}{16}$  litre of glycerine,  $\frac{1}{2}$  litre of boiling water, and 140 grams of magnesia (made into a milk with  $\frac{1}{2}$  litre of water) are mixed with  $\frac{3}{4}$  litre of gum water (500 grams to the litre), and printed, steamed, and washed in the usual way (W. J. 1872, 709).

The following substances have been found to constitute coralline:—

(1) **Aurine** (*pararosolic acid*)  $C_{10}H_8O_3$  or  $(OH.C_6H_4)_2.C<\begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix}>$  (compare, however, Armstrong, C. S. Proc., No. 49, p. 30). Aurine occurs in coralline, and is probably formed according to the equation

$3C_6H_5O + H_2C_2O_4 = C_{10}H_8O_3 + H_2CO_3 + 2H_2O$   
(D. and S., A. 196, 79; compare, however, Zulkowsky, A. 202, 184; E. and O. Fischer, B. 11, 201; Gukassianz, B. 11, 1179; Z., B. 11, 1431; Nencki and Schmid, J. pr. [2] 25, 273); Z., M. 5, 108; Staub and Smith, B. 17, 1740).

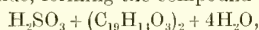
**Preparation.**—Zulkowsky (A. 194, 123; 202, 185) gives the following method for the pre-

paration of coralline and the isolation of its constituents. A mixture of phenol (10 parts) and sulphuric acid of 66°B. (5 parts) is heated with anhydrous oxalic acid (6-7 parts) at 120-130° until the mass becomes viscid and the evolution of gas small. About 24 hours is usually required for this stage of the process, and the yield of coralline varies between 60 and 70 p.c. The product whilst still hot is poured into so much water that further addition of water does not produce a precipitate. In this way the greater part of the coralline is separated from the unattacked phenol and phenolsulphonic acid which, together with sulphuric acid and a small quantity of coralline, remain in solution and can be made to yield a further quantity of the colouring matter by removing the sulphuric acid with lime, evaporating the filtrate and again heating with oxalic acid. To free it from adhering phenol, the precipitated coralline is repeatedly boiled with water (heated by means of steam). It is then powdered, dissolved in warm dilute soda ley, and the solution, when cold, saturated with sulphur dioxide, which decolourises it and produces a white, flocculent precipitate; water is then added so long as a white precipitate forms, and after standing for five to six days to complete the separation, the whole is filtered from the precipitated resinous corallinephthalin (pseudorosolic acid) which forms about 70 p.c. of coralline. To separate aurine the filtrate is heated to 70-80°, and an excess of hydrochloric acid added, which precipitates the crystallisable rosolic acids in the form of double compounds with sulphurous acid as a red mass. This is filtered off, washed, heated at 100° to remove all sulphur dioxide, dissolved in 60 p.c. alcohol in the proportion of 1 kilo. of the product to 6.5 kilos. of alcohol, and the solution allowed to crystallise until red streaks appear on its surface; the crystalline separation, consisting chiefly of methylaurine and constituting about 21.5 p.c. of the portion soluble in alcohol, is then filtered off through a platinum cone without the use of filter-paper, and washed with 50 p.c. alcohol. On saturating the mother liquor with sulphur dioxide and allowing it to stand until red streaks appear on the surface, a second fraction is obtained amounting to 22.5 p.c., which consists of aurine in the form of a double compound with sulphurous acid, and loses all sulphur dioxide on heating. The mother liquor is then freed from alcohol by evaporation on a water-bath, the residue dissolved in soda ley, and the solution saturated with sulphur dioxide in order to separate the lenkorosolic acid (12.5 p.c.), which, mixed with some resin, forms a bright-red crystalline powder. Hydrochloric acid is then added to the filtrate, whereby a further quantity of methylaurine (3.4 p.c.) separates accompanied with much resin which is removed by dissolving the precipitate, after it has been heated to remove sulphur dioxide, in absolute alcohol and saturating the solution with gaseous ammonia; after some days steel blue needles of methylaurine-ammonia crystallise out. The various crystalline precipitates are then purified by repeated crystallisation from 60 p.c. alcohol. It should be noted that in these papers reference is made to a fourth compound, 'oxidised aurine' as a constituent of coralline; later

investigation has, however, shown that the so-called oxidised aurine is nothing more than impure aurine sulphate (Zulkowsky, M. 3, 465).

To obtain aurine from the commercial product, Dale and Schorlemmer (A. 166, 280) treat a concentrated alcoholic solution of coralline with gaseous ammonia until crystals of the compound of aurine with ammonia cease to form; the precipitate is then heated with hydrochloric acid or acetic acid to remove ammonia and the product repeatedly crystallised from alcohol. A second method, in which the commercial product is washed with cold alcohol and the residue repeatedly crystallised from alcohol, has also been described (D. and S., A. 196, 77).

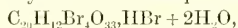
*Properties.*—Aurine crystallises in garnet red rhombic forms, which appear rose-red by transmitted, and show a sky-blue lustre by reflected light. It does not melt at 220°, and is insoluble in water, but soluble in alcohol and acetic acid to yellow-red, and in alkalis and ammonia to carmine solutions. Aurine combines with sulphur dioxide, forming the compound



which crystallises in red cubes and cubic octahedra, showing a green metallic lustre (D. and S., A. 166, 184; Z., A. 202, 200); it also combines with alkaline bisulphites (D. and S.). Acetic anhydride converts it into the *acetyl*-derivative,  $\text{C}_{19}\text{H}_{11}\text{O}_3\cdot\text{C}_2\text{H}_3\text{O}_2$ , and bromine reacts with it in acetic acid solution to form *tetrabromaurine*,  $\text{C}_{19}\text{H}_9\text{Br}_4\text{O}_3$ , which yields violet solutions with alkalis, and in acid solution is a dark-violet dye for silk and wool (D. and S., A. 196, 81; compare Z., M. 3, 465; Ackermann, B. 17, 1624). When an alcoholic solution of aurine is saturated with ammonia, *aurine-ammonia*  $\text{C}_{19}\text{H}_{11}\text{O}_3\cdot(\text{NH}_3)_3$  is obtained; this crystallises in dark-red needles, and rapidly loses ammonia on exposure to air. If, however, aurine is heated with aqueous or alcoholic ammonia at 180-200° for 20 hours it yields *para*leukaniline (D. and S., A. 196, 75); and similar treatment with methylamine and aniline results in the formation of trimethyl- and triphenyl-rozaniline respectively. Reducing agents, and zinc-dust with acetic acid in particular, convert it into *para*leukaurine  $\text{CH}(\text{C}_6\text{H}_4\cdot\text{OH})_3$ , which crystallises from alcohol in colourless lustrous needles, does not melt at 130°, yields a *tri*acetyl-derivative melting at 138-139°, and on oxidation with permanganate or ferricyanide of potassium does not yield aurine, but an undetermined red product (D. and S., Z.; G. and C.).

The following homologues of aurine have been prepared by Nencki (J. pr. [2] 25, 275): *eresolaurine*,  $\text{C}_{27}\text{H}_{20}\text{O}_2$ ; *resaurine*,  $\text{C}_{19}\text{H}_{11}\text{O}_6$ ; and *oreinolaurine*,  $\text{C}_{22}\text{H}_{15}\text{O}_2$ .

(2) *Methylaurine*  $\text{C}_{20}\text{H}_{16}\text{O}_4$  (for isolation *v. Aurine*) crystallises in small brick-red crystals with a green metallic lustre, and does not melt at 200°. Bromine in acetic acid converts it into brassy crystals of the composition



which on boiling with water yield *tetrabromo-methylaurine*; this dissolves in alcohol with a violet-red, and in alkalis with a magenta colour. On reduction with zinc-dust and acetic acid, methylaurine yields the *leuko*-base  $\text{C}_{20}\text{H}_{18}\text{O}_3$ ,



crystallising in colourless rhombic needles (Z., l.c.; M. 3, 471).

(3) **Pseudorosolic acid** (*corallinephthalin* or *phenolcoralline*)  $C_{20}H_{16}O_4$  is, together with other amorphous substances, the chief constituent of coralline. In colour it is red, with a green metallic lustre, and on oxidation with potassium permanganate yields corallinephthalin (Z.).

(4) In addition to the foregoing, **phenyl ortho-oxalate**  $C_{14}H_{10}O_6$  sublimes during the preparation of aurine, and is found on the lids of the aurine pots in the form of colourless needles, melting at  $128^\circ$ . It plays no part, however, in the formation of aurine, but is produced by the action of phenol vapour on anhydrous oxalic acid (Claparède and Smith, C.S. 1883, 358; Staub and Smith, B. 17, 1740).

**Pænone** (*red coralline* or *aurine R.*) is prepared by heating 2 parts of (yellow) coralline and 1 part of aqueous ammonia (sp.gr. = 0.91) in an autoclave at  $125$ – $140^\circ$ , until a test shows the desired shade; the product is then poured into water acidified with sulphuric acid.

Pænone is a dark-red amorphous mass, with a green metallic lustre, and is a mixed product containing among other bodies some pararosaniline. It is insoluble in water, but soluble in alcohol and alkalis yielding purple-red solutions; acids do not affect the colour of its solutions. With wool and silk it gives shades intermediate between those of magenta and cochineal, and in dyeing a bath prepared according to Schröder's directions for coralline is employed. For printing, 10 parts of pænone are dissolved in 40 parts of alcohol, and the solution thickened with 225 parts of casein solution (100 grams casein, 300 grams water, and 20 grams ammonium chloride).

**Azuline** or **Azurine**. A blue colouring matter obtained by heating yellow coralline with aniline (D. and S., A. 166, 294; Guinon, Marnas and Bonnet, l.c.).

**Rosolic acid** (*rosaurine*)  $C_{20}H_{16}O_3$  or  $OH.C_6H_3(CH_3).>C<\begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix}>$  is formed by diazotising rosaniline (Caro and Wanklyn, C. N. 14, 37).

**Preparation.**—500 grams of rosaniline, or the corresponding quantity of a rosaniline salt, are dissolved in  $1\frac{1}{2}$  litre of concentrated hydrochloric acid diluted with  $1\frac{1}{2}$  litre of water, and the filtered brownish-yellow solution diluted with 150 litres of water and treated with a dilute solution of sodium nitrite until the rosaniline has almost but not quite disappeared. The whole is then heated gradually to boiling, and filtered after the evolution of nitrogen has ceased. On cooling, rosolic acid separates in lustrous brownish-green crystals, and is purified by dissolving in soda ley, saturating the solution with sulphur dioxide, filtering and precipitating the compound by addition of a mineral acid to the nearly colourless filtrate. Purification from inorganic salts is best effected by solution in alcohol and precipitation with water (Graebe and Caro, A. 179, 192).

**Properties.**—Rosolic acid crystallises from dilute alcohol in ruby-red crystals, or in greenish scales with a metallic lustre, does not melt at  $270^\circ$ , and is insoluble in benzene and carbon bisulphide, very sparingly soluble in water,

soluble in ether and acetic acid, and readily soluble in alcohol. In alkalis it dissolves with a red colour, which in very thin layers is bluish-red, and in thick layers is yellowish-red. It is a feeble acid, and yields an unstable ammonium salt, crystallising in steel-blue needles. Bromine in acetic acid solution converts it into *tetrabromorosolic acid*  $C_{20}H_{12}Br_4O_3$ , which crystallises in lustrous green scales, dissolves in alkalis with a violet colour, and with reducing agents yields the *leuko*-compound. When heated with acetic anhydride at  $150$ – $200^\circ$  it forms, among other compounds, triacetylleukorosolic acid (m.p. =  $148$ – $149^\circ$ ); *leukorosolic acid*  $C_{20}H_{16}O_3$  itself being obtained by reducing rosolic acid either with sodium amalgam or with zinc-dust and soda ley (G. and C.).

Closely related to aurine is *benzaurine* or *phenolbenzëin*  $C_{19}H_{11}O_2$  or  $\begin{smallmatrix} C_6H_5 \\ OH.C_6H_3 \end{smallmatrix}>C<\begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix}>$

obtained by gently heating 1 mol. of benzotrichloride with 2 mols. of anhydrous phenol, removing excess of phenol by steam distillation, extracting the residue with sodium bisulphite, and precipitating the filtrate with hydrochloric acid (Doebner, B. 12, 1462; compare Homolka, B. 18, 988). It crystallises in brick-red crystals, melts at about  $100^\circ$ , is insoluble in water, but soluble in alcohol, ether, and acetic acid. Alkalis dissolve it, yielding violet solutions. The *acetyl*-derivative melts at  $119^\circ$ . On reduction with zinc and hydrochloric acid, benzaurin is converted into dihydroxytriphenylmethane  $C_{18}H_{15}O_2$ .

**Resorcinolbenzëin**  $C_{13}H_9O_3$  (Doebner, B. 13, 610; A. 217, 234; Actiengesellschaft für Anilinfabrikation in Berlin, Germ. pat. 4322, Feb. 26, 1878) is obtained by heating 1 mol. of benzotrichloride and 2 mol. of resorcinol at  $180$ – $190^\circ$ . It crystallises in large violet-red prisms, appearing yellow by transmitted light, is insoluble in water, ether, and benzene, has a yellowish-green fluorescence in dilute alcoholic solution, and yields a *bromo*-derivative which is sparingly soluble in all ordinary solvents, and dyes wool and silk in shades similar to those produced by eosin. W. P. W.

**AURUM MUSIVUM** or **MOSAICUM**. *Mosaic gold*. Made by triturating an amalgam of 2 parts tin and 1 of mercury with 1 part sal ammoniac and 1 of sulphur, and subsequently subliming. It is used as a bronzing powder for plaster figures.

**AUSTRALENE** v. TURPENTINE.

**AUSTRIAN CINNABAR**. *Basic lead chromate* (v. CHROMIUM).

**AUTOCLAVE**. An apparatus constructed on the principle of Papin's digester, for heating liquids at temperatures above their boiling points. In the manufacture of coal-tar colours large autoclaves of copper, or, more frequently, of cast or wrought iron, occasionally enamelled within, and capable of withstanding very high pressure, are employed. They are fitted with a pressure-gauge and safety valve, and tubes for the insertion of thermometers, and are usually closed by a screw or flanged cover, working against a leaden washer, and are heated either in oil or in a bath of molten lead. As they have frequently to sustain pressures of from 20 to 30 atmos., they are tested before use by



hydraulic pressure. Occasionally they are provided with agitators working through stuffing boxes, in order to ensure thorough mixing of the contents when heated.

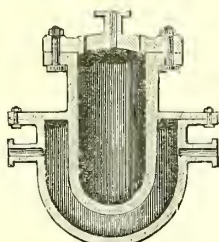


FIG. 1.

Fig. 4 shows a method of withdrawing portions of the contents of an autoclave, or adding liquid

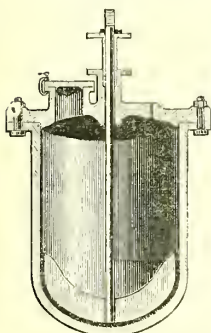


FIG. 2.

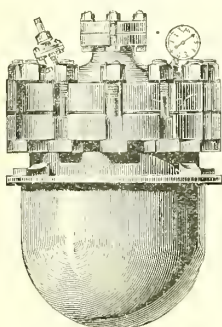


FIG. 3.

without removing the cover, when the apparatus is in use. The three-way valve *a* is adjusted

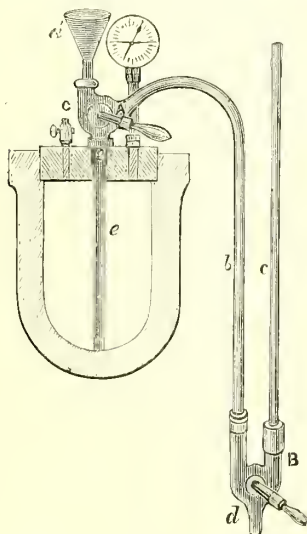


FIG. 4.

so as to prevent passage through the pipe *e*. In order to withdraw a sample the three-way cock *b* is made to communicate with *b* and *d*, and

the valve *a* turned with a jerk so as to connect *c* with *b*; the sample is then withdrawn at *d*. To completely remove the charge the valve *a* is left open for some time. In working without pressure the air-cock *c* is opened, and communication established between *b* and *e* and *a'* and *b*; *b* and *c* are then filled with liquor identical in constitution with that contained in the apparatus obtained from a previous operation. The contents of the vessel are then removed by restoring the communication between *e* and *b* and *b* and *d*. To introduce liquor into the apparatus without removing the cover, the air-cock *c* is opened, and the funnel *a'* made to communicate with the pipe *e* by regulating the valve *a*.

**AUTUNITE** or **URANITE**. A mineral found at Autun, containing 14.00 p.c.  $P_2O_5$ , 59.00  $M_2O_3$ , 5.8 CaO, 21.2 OH, (Pisani, C. R. 52, 817).

**AVA** or **KAVA-KAVA**. The root of *Piper methysticum*, growing in the islands of the Pacific. It is taken as an intoxicant by the natives, and is used as a drug on the Continent. It is often adulterated with matico and annatto (Ph. [3], 7, 149).

**AVENTURINE**. A variety of quartz found at Capa de Gata, Spain, spangled throughout with minute yellow scales of mica, is known as aventurine quartz. An aventurine felspar or sunstone is found at Tvedestrand, Norway. It is used for ornaments.

*Artificial aventurine*, or glass, or gold flux, was manufactured for a long period at the glass-works of Murano, near Venice. It may be prepared by adding to 100 parts of a not too refractory glass, 8 to 10 parts of a mixture of equal parts of ferrous and cuprous oxides, and allowing the mixture to cool very slowly so as to facilitate the formation of crystals.

*Aventurine glaze* for porcelain, invented by Wöhler (A. 70, 57), is prepared by finely grinding 31 parts Halle kaolin, 43 quartz sand, 14 gypsum, and 12 porcelain fragments; making the whole into a paste with 300 parts water, and adding successively 19 parts potassium dichromate, 47 lead acetate, 100 ferrous sulphate, and sufficient ammonia to precipitate the whole of the iron. After the soluble potash and ammonium salts have been washed out the glazing is ready for use.

**AVIGNON GRAINS**. The seeds of *Rhamnus insectorius*, employed in dyeing for the production of yellow colours *v. Rhamnin*, art. XANTHORAMIN.

**AVOCADO-PEAR, OIL OF**. An oil obtained from the oleaginous fruit of the *Persea gratissima*. Hofmann stated that for the purposes of the soapmaker this oil would be as valuable as palm oil.

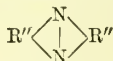
**AWAL** or **TURWAR**. An Indian drug, the bark of *Cassia auriculata* (Dymock, Ph. [3] 7, 977).

**AWLA** *v. AMLAKI*.

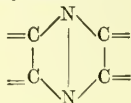
**AZADIRACHTA, MARGOSA, or NIM**. The bark of the nim tree (*Azadirachta indica*) is commonly used in India as a tonic and febrifuge. It contains a bitter resin. An oil, used in medicine and for burning, is expressed from the seeds, which on saponification yielded 35 p.c. of fatty acid melting at 30°, and 65 p.c. melting at 44°C.

**AZARINE** *v. AZO-COLOURING MATTERS*.

**AZINES AND COLOURING MATTERS DERIVED FROM THEM.** The name azines has been given to substances built up on the type

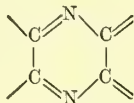


R'' being a bivalent radicle belonging to either the fatty or aromatic series, and containing two free valencies on two connected carbon atoms. Consequently every azine contains the group

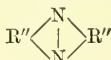


and it is from this group that the large number of azines derive their striking and characteristic properties.

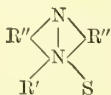
Several azines have been known for many years, without, however, their constitution being understood. Hinsberg (B. 18, 319), who discovered a general method for preparing such compounds, called them quinoxalines, and believed their constitution to contain the molecular group



which was shown by Witt to be highly improbable (B. 19, 915; C. J. 1886, 913). The term azine was first used by Merz (B. 19, 725), who also first used the formula containing connected nitrogen atoms. Several new and general methods for the production of compounds of this class were discovered by Merz (*l.c.*) and by Witt (B. 19, 917; 20, 571). The latter also proved (B. 19, 447) that the characteristic azine group



possesses chromophoric properties, and that consequently every azine is a chromogene whose amido- and oxy-derivatives are, of necessity, colouring matters. The amido-derivatives of azines were first prepared by Witt, who gave them the generic name of eurhodines (B. 19, 441; 21, 2420), whilst the name of eurhodols was assigned to the corresponding hydroxy-derivatives. Later on it was shown by Bernthsen (B. 19, 2690) and Nietzki (B. 19, 3017) that the old and well-known saffranine group of colouring matters, whose similarity to the eurhodines had already been mentioned by Witt (B. 19, 441), was closely allied to them and similarly constituted. The correct constitutional formula of pheno-saffranine was established by Witt (B. 19, 2791). The saffranines stand in a relation to the eurhodines similar to that existing between amines and ammonium bases; they are the amido-derivatives of the azonium bases, substances of the typical constitution



in which R' stands for any monovalent organic

radicle and X for any acid group, such as, for instance, Cl, NO<sub>3</sub>, &c. These azonium bases, which at first were hypothetical, have since been prepared by the same author (Witt, B. 20, 1183). Their oxy-derivatives have been prepared by Nietzki and Otto (B. 21, 1736), and received the name of saffranols.

Of all these substances the saffranines are the most important. A considerable number of them are prepared on a large scale and used as dyes. The eurhodines are less valuable, although a few of them have found practical application, whilst the saffranols, eurhodols, and the azines and azonium bases themselves are only of theoretical interest.

**Azines.** These bases have been obtained by the following methods:

1. By heating  $\alpha$ -nitronaphthalin with powdered quicklime, Laurent (Gm. 7, 24) obtained a substance which he called *naphthase*. The same compound was prepared by Doer (B. 3, 291) and by Klobukowski (B. 10, 573) who employed zinc-dust instead of quicklime. This compound was proved to be dinaphthazine by Witt (B. 19, 2791).

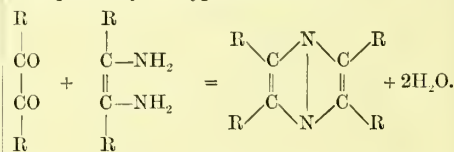
2. The same substance was prepared by Schichuzky (J. R. 6, 2464) by distilling  $\alpha$ -naphthylamine over heated lead oxide.

3. Diphenazine (azophenylene) was first obtained by Claus (A. 168, 1) by the dry distillation of orthoazobenzoic acid in the shape of its calcium or potassium salts.

4. A general method for the production of azines was indicated by Hinsberg (B. 17, 319; 18, 1228) who showed that whenever orthodi-

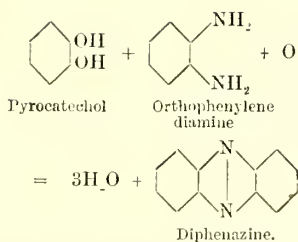
ketones (compounds containing the group  $\begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array}$ ) re-

acted on orthodiamines, two molecules of water were given off and an azine (quinoxaline) was the result. The first chemist who applied this reaction was Aguiar (Trans. Portuguese Acad. Sci. 2, 313; B. 7, 312) who, however, did not recognise its mechanism. This reaction may be interpreted by the typical formula



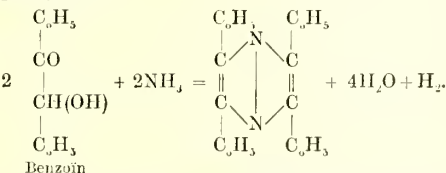
This method is so simple and works in most cases so well, that it has been recommended by Hinsberg (A. 237, 343, 371) as an easy and, in fact, as the best method of identifying either an orthodiamine or an orthodiketone. Very small quantities of the ingredients are as a rule sufficient to obtain the characteristic azine, which may be easily identified by its melting-point and sulphuric acid reaction.

5. A similar method, indicated by Merz (B. 19, 725), is of less general application, as it may only be applied to the production of purely aromatic azines. It consists in the reaction of orthodihydroxyl-derivatives of aromatic hydrocarbons upon aromatic orthodiamines. In this reaction the hydro-derivatives of the azines are formed, which, however, are easily transformed by the oxygen of the air into the azines themselves:

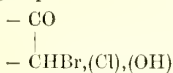


6. Azines may also be prepared by heating  $\alpha$ -diketones with ammonia or ammonium acetate. This method has been applied to the production of diphenanthrazine from phenanthraquinone by Japp and Wilson (C. J. 1886, 826) and of dinaphthazine from  $\beta$ -naphthaquinone by Japp and Burton (C. J. 1887, 98).

7. Japp and Wilson showed (*loc.*) that benzoin—an  $\alpha$ -hydroxyketone—when heated with ammonia or ammonium acetate, yielded tetraphenylazine:

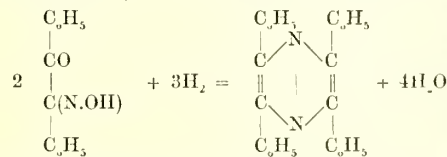


This reaction was afterwards extended by L. Wolff, who showed (B. 21, 123) that compounds containing the group

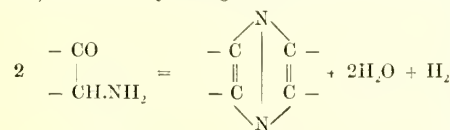


are converted by ammonia into azines.

8. A reaction related to the foregoing is that in which the compounds described by V. Meyer as 'ketines' or 'alkines' (azines) are formed by the reduction of the monohydroximes of  $\alpha$ -dicarboxyl-compounds in alkaline solution. Thus benzil-monohydroxime, when dissolved in caustic soda and treated with sodium amalgam, gives tetraphenylazine (*tetraphenylaldine* in V. Meyer's nomenclature):



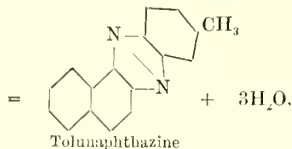
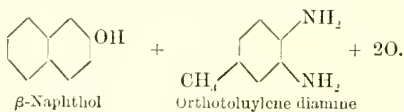
(Braun and V. Meyer, B. 21, 1296). If, however, the reduction of such a monohydroxime is carried out in acid solution, the hydrochloride of an unstable base—probably an  $\alpha$ -amido-ketone—is obtained, which, when liberated from its salts, readily parts with hydrogen (probably by oxidation) and water, yielding an azine:



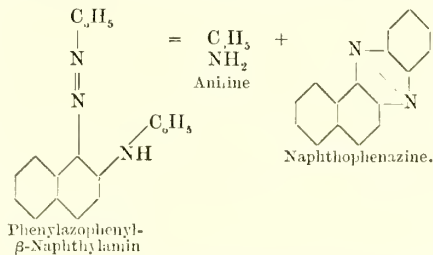
(Braun and V. Meyer, B. 21, 1947).

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9. Another mode of formation of the azines consists in the joint oxidation of certain phenols with aromatic orthodiamines. This method was applied to the production of tolunaphthazin by Witt (B. 19, 917).



10. A very peculiar mode of formation of these substances was discovered by Witt (B. 20, 571), who showed that the azo-derivatives of secondary  $\beta$ -naphthylamines are decomposed by being heated with strong acids into the corresponding azine and amido-compound, thus:



11. Finally a pyrogenic formation of an azine may be mentioned, which has been published by Berthsen (B. 19, 3256), although only traces of phenazine were found. It consists in distilling aniline through red-hot tubes, when, according to the author small quantities of phenazine may be isolated from the tar which is the chief product of the reaction.

All azines have certain peculiar properties in common. As a rule they are solid, well-crystallised compounds of a pale yellow or orange colour, possessing a high melting-point and boiling at very high temperatures without the slightest decomposition. They sublime at temperatures below their boiling-point, and their vapour condenses into voluminous flakes of a crystalline structure.

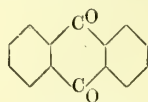
All the azines are bases which form salts with mineral but not with organic acids. These salts, which are generally of a deep red or orange colour, are easily decomposed by water, the free azine being liberated. All azines dissolve, with characteristic intense colourations, in concentrated sulphuric acid. These colourations are no doubt due to the formation of diacid salts which are stable only in the presence of an excess of concentrated sulphuric acid. If, therefore, water be added to the coloured solution of an azine in sulphuric acid, an instantaneous change is the result: the yellow or orange mono-acid salt is formed, and on further addition of water the free azine itself separates in flakes.

Q

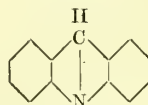


These striking colour reactions are highly characteristic and, therefore, furnish the best means of identifying the azines.

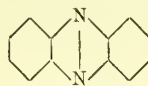
Notwithstanding these intense colourations the azines are not colouring matters, they only become such by the introduction of an amido- or a hydroxy- group into the molecule. The azines are chromogenes, and in this respect strictly analogous to anthraquinone and acridine, to which they bear a strong resemblance in constitution:



Anthraquinone

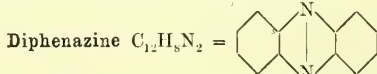


Acridine



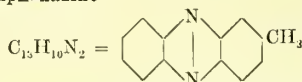
Phenazine.

The following is an enumeration of the more important aromatic azines from which well-known colouring matters are derived:



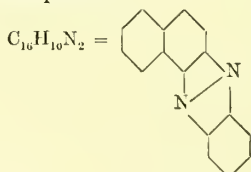
(Claus, A. 168, 1; Bernthsen, B. 19, 3256; Ris, B. 19, 2206) has been obtained by the methods 3, 5, and 11. It forms pale yellow needles, of the m.p.  $170-171^\circ$ , soluble in alcohol and most other solvents. It distils without decomposition. It dissolves in strong acids, forming unstable salts of a red colour.

#### Toluphenazine



has been prepared by Merz (B. 19, 725) by the action of pyrocatechol on orthotoluylenediamine. It is very similar to diphenazine. Its m.p. is  $117^\circ$ , its b.p.  $350^\circ$ .

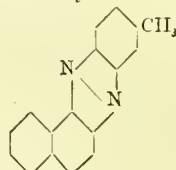
#### Naphthophenazine



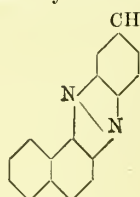
has been prepared by Witt (B. 20, 571). The best mode of obtaining it is by the decomposition, by acid, of the azo-compounds derived from phenyl- $\beta$ -naphthylamine, but it has also been prepared by the action of  $\beta$ -naphthaquinone on orthophenylenediamine and by simultaneous oxidation of the latter and  $\beta$ -naphthol. It forms yellow needles, melting at  $142.5^\circ$ , distilling at a high temperature without decomposition, and

dissolving in sulphuric acid with a reddish-brown colouration. On dilution, two sulphates crystallise from this solution. It is supposed that the formation of two series of monacid salts of this base is due to either of the two nitrogen atoms becoming pentavalent and saturated with the acid.

**Tolunaphthazines**  $C_{17}H_{12}N_2$ . Three substances of this formula are known, the isomerism of which has been discussed by Witt (B. 20, 577). One of these, melting at  $179.8^\circ$  has been prepared by the simultaneous oxidation (B. 19, 917) of orthotoluylenediamine and  $\beta$ -naphthol. Its constitution is expressed by the formula



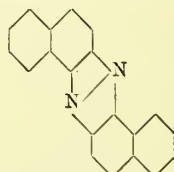
It dissolves in sulphuric acid with a violet colouration. The other is formed by the decomposition by acids of the azo-derivatives of paratolyl- $\beta$ -naphthylamine (B. 20, 577). Its constitution is represented by the formula



Its melting-point is  $169^\circ$ , its sulphuric acid reaction similar to that of naphthaphenazine. The third tolunaphthazine, discovered by Hinsberg (A. 237, 343a, 371), has been proved to consist of a molecular combination of the two preceding ones; its melting-point is  $139-42^\circ$ .

Several other tolunaphthazines are theoretically possible. They have not, however, hitherto been prepared.

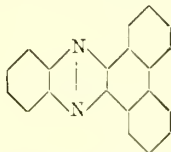
**Dinaphthazines**  $C_{20}H_{12}N_2$ . Several isomerides of this formula are possible, only one of which has been prepared hitherto by various methods already mentioned. This substance, which was originally discovered by Laurent (Gm. 7, 24), and described under the name of naphthase, has the constitutional formula



It forms long g"stening needles of pale orange colour, melting at  $275^\circ$ , and dissolving in sulphuric acid with an intense violet colouration.

**Phenophenanthrazine**  $C_{20}H_{12}N_2$  (isomeric with dinaphthazine). Of the large number of azines prepared from phenanthraquinone and aromatic orthodiamines, only this and the two following may be mentioned as typical. It may be obtained by acting on orthophenylenediamine with either

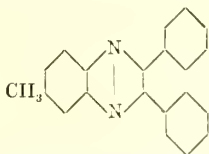
phenanthraquinone in an acetic acid solution (Hinsberg, A. 237, 340) or with phenanthraquinone sodium bisulphite in an aqueous solution. It crystallises in pale yellow needles, melting at 217°, and dissolves in sulphuric acid with a beautiful red colouration. Its constitution is



A similar substance may be obtained from orthotoluylenediamine. It melts at 212-213°.

**Phenanthronaphthazine**  $C_{24}H_{11}N_2$  is easily obtained (Lawson, B. 18, 2426) from orthonaphthylenediamine and phenanthraquinone. It gives a violet colouration with sulphuric acid. Melting-point 273°. The sulphonic acid derivatives of this substance,  $C_{24}H_{11}N_2SO_3H$ , are obtained (Witt, B. 19, 1719; 21, 3485 *seq.*) by acting with an aqueous solution of phenanthraquinone sodium bisulphite upon the solutions of the various naphthylenediamine sulphonic acids in sodium acetate solution, acidulated with acetic acid. These sodium salts are soluble in pure water; small quantities of alkaline salts are sufficient to precipitate them from these solutions.

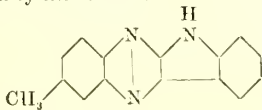
**Diphenyltoluazaine**  $C_{24}H_{11}N_2$  may be mentioned as a type of the many azines obtained by the action of benzil on aromatic amines. It separates out (Hinsberg, A. 237, 340) in silvery leaflets from an alcoholic solution of benzil mixed with a solution of orthotoluylenediamine. It melts at 111°, and dissolves with a crimson shade in sulphuric acid. Its constitution is expressed by the formula



The corresponding derivative of orthonaphthylenediamine has been prepared by Lawson (B. 18, 2426).

**Chrysonaphthazine**  $C_{25}H_{16}N_2$  and **Chrysonaphthazine**  $C_{28}H_{18}N_2$  have been prepared by Liebermann and Witt (B. 20, 2442) from chrysoquinone and the corresponding orthodiamines. The same authors obtained azine derivatives from the quinone of pice.

**Toluindazine**  $C_{11}H_{11}N_3$ , the azine derivative of isatine, has been prepared by Hinsberg (A. 237, 344) from orthotoluylenediamine and isatine, by melting together the ingredients and crystallising the product obtained from a mixture of alcohol and acetic acid. It forms yellow needles, melting at 290°, and dissolving in acids with a brownish-red colouration. Its constitution is expressed by the formula



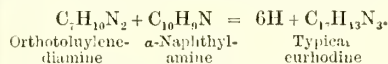
A large number of other less important azines have been prepared in experiments made with a view to showing that certain compounds obtained by the authors were either orthodiketones or orthodiamines.

**Colouring matters derived from azines (eurrhodines and eurhodols).**

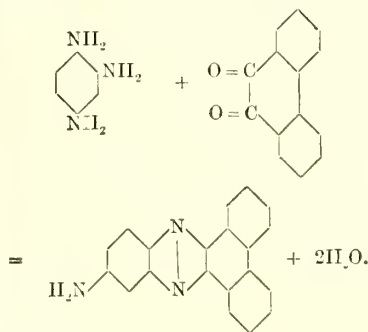
It has already been said that by the introduction of an auxochromic group,  $NH_2$  or  $OH$ , into the molecule of an azine, the latter is transformed into a colouring matter. The amido-derivatives of azines containing either one or several amido-groups are embraced by the generic name of *eurrhodines*, whilst the name of *eurhodols* has been given to the phenolic ( $OH$ ) derivatives of the azines. The following is an enumeration of the various methods by which eurrhodines and eurhodols have been obtained.

#### A. EURRHODINES.

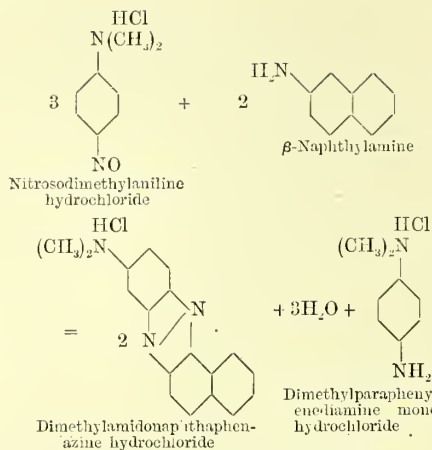
1. By heating together any orthamido-azo-compound and the hydrochloride of certain aromatic monamines, such as, for instance,  $\alpha$ -naphthylamine or  $\alpha$ -amidoquinoline, preferably in a phenol solution, monamido-azines (the eurrhodines proper) are obtained. It was by this process that the first eurrhodine was discovered by Witt in 1883 (B. 18, 1119; 19, 441) by heating orthamidooztoluene with naphthylamine hydrochloride. In this reaction an orthodiamine is formed by the reduction of the amido-azo-compound, which combines with the  $\alpha$ -naphthylamine, hydrogen being eliminated and absorbed by the amido-azo-compound still present.



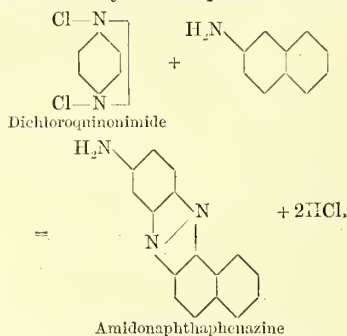
2. Another method of much greater applicability consists in reacting with  $\alpha$ -diketones upon aromatic triamines, which contain two amido-groups in the ortho-position. Two molecules of water are eliminated for every molecule of eurrhodine formed. Thus, for instance, a eurrhodine was obtained from triamidobenzene and phenanthraquinone (Witt, B. 19, 445):



3. Another method of considerable applicability consists in heating together nitrosamines (Witt, B. 21, 719) or quinonedichlorimides (Nietzki a. Otto, B. 21, 1598) with aromatic amines in which the para-position to the amido-group is occupied by some radicle. Thus, for instance, a eurrhodine is formed by heating together nitrosodimethylamine hydrochloride and  $\beta$ -naphthylamine, in an acetic acid solution,

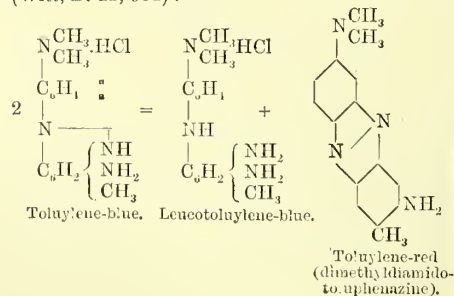


and an analogous, though somewhat different reaction takes place if the nitrosodimethylaniline be substituted by dichloroquinonimide.



4. Eurhodines proper may also be obtained by the reduction (with ammonium sulphide) of nitro-azines. Thus, for instance, nitrophenanthrazine may be reduced into the eurhodine amidophenanthrazine (Heim, B. 21, 2306).

5. Diamidoazines are formed by the spontaneous decomposition of certain indamines, if their solutions be boiled for a certain time. Thus toluylene blue, the indamine produced by the action of nitrosodimethylaniline hydrochloride upon metatoluylenediamine, is decomposed if its solution be boiled for some time, dimethyldiamidotoluphenazine (toluylene-red) being the principal product of this reaction (Witt, B. 12, 931):

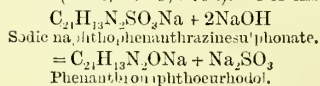


6. Di- and polyamido-azines may also be prepared by the oxidation of orthodiamines and of polyamines containing two amido-groups in the ortho-position. Thus O. Fischer and E. Hepp proved (B. 22, 355) that the red substance which is formed by the oxidation of orthophenylenediamine and which has been observed by many investigators (Griess, B. 5, 292; Salkowski, A. 173, 58; Rudolph, B. 12, 2211; Wiesinger, A. 224, 353), is nothing else than diamidophenazine. And Nietzki and Müller obtained (B. 22, 447) by oxidising tetramidobenzene with a current of air tetramidophenazine.

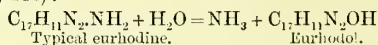
#### B. EURHODOLS.

These may likewise be prepared by various methods.

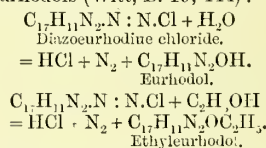
1. The sulphonic acids of azines, fused with potash, readily yield the corresponding oxyazines or eurhodols (Witt, B. 19, 2791). For instance:



2. Several eurhodines (amido-azines) yield the corresponding eurhodol on being heated under pressure with strong acids, a hydrolysis taking place under the circumstances (Witt, B. 19, 444):



3. Diazo-azines, on being boiled with water, yield the corresponding eurhodols; on being boiled with alcohol they yield the alkylic ethers of these eurhodols (Witt, B. 19, 444):



The following is an enumeration of those of the eurhodines and eurhodols which have been more closely investigated, the properties of which are typical for the whole class of colouring-matters.

**Typical eurhodine**,  $\text{C}_{17}\text{H}_{11}\text{N}_3$  (Witt, B. 19, 445).

The mode of formation of this substance has already been given (Section A, 1). It is best prepared by heating equal molecules of orth-amidoazotoluene, of the melting-point  $118.5^\circ$ , and  $\alpha$ -naphthylamine hydrochloride, dissolved in phenol to  $130^\circ\text{C}$ ., until the colour of the mixture, which is at first of an emerald green, has changed into a brilliant scarlet. The mixture is now treated with a large quantity of toluene, when the hydrochloride of the new dyestuff is precipitated in a crystalline state. By recrystallisation from water acidulated with hydrochloric acid it may be obtained in a pure state. From the pure hydrochloride the free eurhodine base is precipitated by alkalis or ammonia in the shape of a yellow powder, which may be recrystallised from aniline. Thus prepared, it forms glistening yellow prisms and needles of a dark-brown colour. It dissolves in ether with a yellow colour and a magnificent green fluorescence, which is characteristic for all the members of this group of dyestuffs. Eurhodine forms three series of salts, of which, however, only those



with one molecule of acid are fairly stable, whilst those containing more acid are decomposed by the addition of water. It is to the formation of these various salts that the peculiar change of colour is due which is observed on adding water to a solution of eurhodine in concentrated sulphuric acid. This solution is of a cherry-red colour. On adding a small quantity of water the colour changes to a fine emerald green, whilst still more water produces the scarlet shade of the normal sulphate. This change of colour, which is observed with all the eurhodines, links them to their parent-substances, the azines, which exhibit similar curious phenomena.

The normal salts of eurhodine are well crystallised and of a bronzed copper colour when solid. In solution they exhibit a bright scarlet tint which they communicate to the fibre. These normal salts are, however, partially decomposed by an excess of water, the free eurhodine base being regenerated. The same takes place if fibres dyed red with eurhodine be washed. The scarlet shade is gradually replaced by the yellow shade of the free eurhodine base. For this reason eurhodine has not found an application in the industry of artificial dyestuffs.

**Amidonaphthophenazine**  $C_{16}H_{11}N_3$  has been obtained by Nietzki and Otto (B. 21, 1598) from  $\beta$ -naphthylamine and dichloroquinonimide. It crystallises in dark-yellow needles. Its salts are of a crimson colour. Its solution in sulphuric acid changes by the addition of water from reddish brown through green into red. It forms a diazo-compound which, when boiled with alcohol, yields the ordinary naphthophenazine, of the melting-point  $142^{\circ}5$ . The following compound is its dimethyl derivative:

**Dimethylamidonaphthophenazine**  $C_{18}H_{13}N_4$  (Witt, B. 21, 719). This eurhodine, the formation of which has been described under Section A, 3, may easily be prepared in quantity by heating together 20 parts nitrosodimethylamine hydrochloride and 10 parts  $\beta$ -naphthylamine with 50 glacial acetic acid; the reaction sets in below  $100^{\circ}C$ , and is apt to become violent. The melt turns a fine violet colour. It is dissolved in water acidulated with hydrochloric acid, and the filtered solution is precipitated by the addition of sodic acetate. The crude eurhodine which is thus precipitated may be purified by dissolving it in alcohol acidulated with hydrochloric acid. From this solution the normal eurhodine hydrochloride crystallises in bronze-coloured needles. From these ammonias liberates the free eurhodine base in the shape of a scarlet crystalline powder. It may be recrystallised from boiling xylene; it is thus obtained in magnificent crystals resembling magnesium-platocyanide, melting at  $205^{\circ}C$ .

The change of colour of a sulphuric acid solution of this eurhodine is not very marked, going from violet through black and green into violet. The ethereal solution of the free base exhibits the brilliant fluorescence characteristic of all eurhodines.

**Amidophenophenanthrazine**  $C_{23}H_{13}N_5$ . This eurhodine was prepared by Witt (B. 19, 445) and by Heim (B. 21, 2366) by the methods given under Section A, 2 and 4. It crystallises from toluene in short, thick, yellow prisms, melting at  $279^{\circ}$ .

**Dimethyldiamidotoluphenazine, Toluylene red**  $C_{15}H_{16}N_4$ . The formation of this compound by the spontaneous decomposition of toluylene-blue has been described under Section A, 5. This azine forms, in a pure state, orange crystals, which contain 4 mol. of water of crystallisation; at  $150^{\circ}$  this is given off and the anhydrous base remains as a dark-red powder. The hydrated base is soluble in ether with a pink colour and a beautiful orange fluorescence. The solution in concentrated sulphuric acid is green; on being diluted with water it changes through sky-blue into red. The normal (monacid) salts are perfectly stable and soluble in water with a pink colour. This solution dyes unmooranted or mooranted cotton and other fibres a pink which in darker shades deepens into a coppery red.

The production of this dyestuff has been patented (Otto N. Witt, G. P. 15,272, dated Nov. 6, 1880). The commercial product, which contains a certain amount of impurities, is sold under the name of 'neutral red.' It is chiefly used in calico-printing, and gives very fast and useful shades.

A similar product is prepared from the indamine which is formed by reacting with nitrosodimethylamine hydrochloride upon metaphenylenediamine. It is embraced by the same patent and sold under the name of 'neutral violet.'

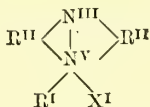
**Typical eurhodol**  $C_{17}H_{11}N_5OH$  (Witt, B. 19, 444). This substance, the formation of which takes place according to the equation given under Section B, 2, forms small leaflets of a yellow or red colour which dissolve in concentrated sulphuric acid with a red colouration, and are reprecipitated from this solution by the addition of water. Caustic soda solution dissolves it with an orange shade. Thus it is shown that this eurhodol (like all compounds of the same class) exhibits both acid and basic properties, the latter being due to the azine group contained in their molecule.

**Eurhodol**  $C_{24}H_{17}N_5OH$ .  $\alpha$ -Hydroxynaphthaphenanthrazine has been obtained (Witt, B. 19, 2791) by the method described under Section B, 1, by the fusion of naphthaphenanthrazine- $\alpha$ -sulphonic acid with caustic potash. Its solution in sulphuric acid is of a fine and intense indigo-blue; it changes very suddenly into red on the addition of water, the sulphate being precipitated. This substance is a fine yellow colouring matter which may be fixed on cotton with alum-mordant, like alizarine. Owing, however, to its costliness it has not been brought into commerce. A large number of isomerides may be prepared by starting from the numerous sulpho-derivatives of orthonaphthylene-diamine, transforming them into azinesulphonates by condensation with pheranthraquinone and into eurhodols by subsequent fusion with caustic alkalis.

**Azonium bases and safranines.** The azonium bases are a class of compounds of which our knowledge is very restricted, only one representative of the class being at present known, and that rather imperfectly. They are, however, of importance, as it is now established beyond doubt that they are the parent substances of the very important class of dyestuffs known as safranines. Although the first artificial dye-

stuff, mauvine, was a true safranin, and although this group of compounds has been frequently under investigation, a correct view of their constitution had not been obtained until quite recently. According to the theory now universally adopted, all safranines are amido-derivatives of azonium bases, to which they stand in the same relation as the azines to the eurhodines. Hydroxy-derivatives of azonium bases have also been prepared and described under the name of safranols. They are, however, of no importance as colouring matters.

The azonium bases themselves, which, as has been said, are with one exception hypothetical, stand in the same relation to the azines as the ammonium bases to the amines. They are azines in which one of the nitrogen atoms has become pentavalent by being saturated with three organic radicles and one acid radicle, the connection with the second nitrogen atom being still preserved by the fifth valency of the pentavalent nitrogen atom. Thus the characteristic constitution of the azonium bases may be expressed by the general formula



in which  $\text{R}^{\text{I}}$  and  $\text{R}^{\text{II}}$  represent mono- and bivalent organic radicles and  $\text{X}^{\text{I}}$  a monovalent acid radicle. The azonium bases are, as far as we know, compounds which possess strong basic properties, and which, in the tenacity with which they retain their acid radicle, strongly resemble the ammonium bases. It is probable that the free azonium bases contain, like the ammonium bases, the hydroxyl group in the position  $\text{X}^{\text{I}}$  of the above general formula.

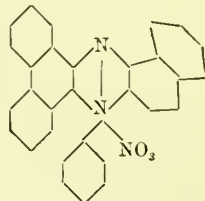
The azonium bases are strongly coloured substances, but their dyeing properties are only developed and brought to perfection by the introduction of amido-groups into their molecule. As the azonium bases theoretically possible are very numerous, and each of them is capable of producing very numerous isomeric mono- and polyamido-derivatives, the number of possible safranines is exceedingly large, and the number of those which have already been prepared is insignificant in comparison with that foreshadowed by theory.

Of the safranines which have hitherto been prepared, only a few are monamido-derivatives of azonium bases. A few more are of doubtful or unknown constitution. The majority are asymmetric diamido-derivatives of azonium bases, containing one amido-group in one of the diatomic organic radicles ( $\text{R}^{\text{II}}$ ) whilst the other is attached to the monatomic radicle ( $\text{R}^{\text{I}}$ ).

The true constitution of phenosafranin and its congeners has been recognised by Witt, who, after pointing out the analogy between the eurhodines and safranines (B. 18, 1119) and clearing up the constitution of the former (B. 19, 446), proved the latter to be asymmetric diamido-azonium bases (B. 19, 3121). Bernthsen's view, who had, basing himself likewise on Witt's eurhodine researches, proposed (B. 19, 2690) somewhat earlier a symmetrical formula for the

safranines, was subsequently proved to be erroneous.

**A. Azonium bases.** Of these only one representative has been hitherto prepared. It was obtained by Witt (B. 20, 1183) by the reaction of phenanthraquinone on phenylorthonaphthylenediamine. By heating these ingredients in an acetic acid solution an intermediate product is obtained, which on treatment with a mineral acid is transformed into the salt of the azonium base.

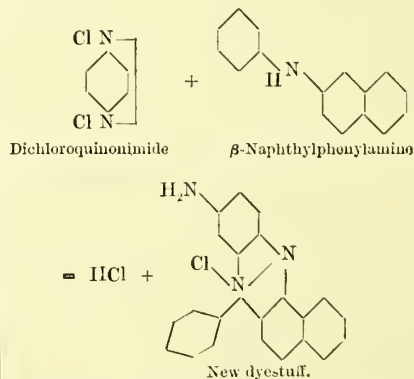


If nitric acid is used the nitrate is deposited in very fine crystals. It is sparingly soluble in water, readily soluble in spirit with a fine orange-red colouration. The hydrochloride dissolves in sulphuric acid with a violet tint, which changes into red on dilution with water.

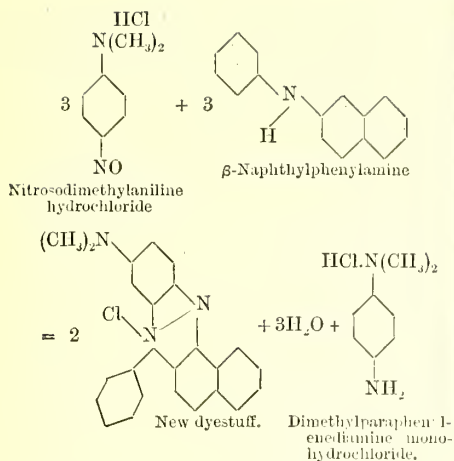
**B. Safranines.** The various colouring-matters belonging to this group have mostly been prepared by various synthetical methods, which may be classed in the following manner:

1. Reduction of the nitro-derivatives of azonium bases. By reacting with mononitrophenanthraquinone and dinitrophenanthraquinone on phenylorthonaphthylenediamine, nitro- and dinitro-derivatives of the above azonium base are obtained, which on reduction with ammonium sulphide yield reddish violet colouring matters belonging to the safranin group (Witt, unpublished observations).

2. By the action of dichloroquinonimides upon secondary aromatic amines, in which the para-position to the amido-group is occupied, monamido-azonium bases are formed (Nietzki and Otto, B. 21, 1598). The reaction for instance between dichloroquinonimide and  $\beta$ -naphthylphenylamine may be represented by the equation:



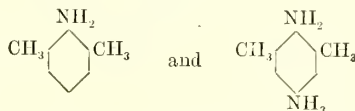
3. In a similar manner nitrosodimethylaniline (or any other nitrosamine) reacts with  $\beta$ -naphthylphenylamine (Witt, B. 21, 719).



Of course any other paradiamine may be substituted for paraphenylenediamine, and any other monamine for aniline. As, however, the formation of an indamine only takes place if the paraposition to the amido-group be still free, it results, that at least one of the two molecules of monamines must fulfil this condition. Thus the formation of a saffranine from paraphenylenediamine takes place on oxidation of one molecule of the diamine with:

- (1) Two molecules of aniline.
- (2) Two molecules of orthotoluidine.
- (3) One of aniline and one of orthotoluidine.
- (4) One of aniline and one of paratoluidine.
- (5) One of orthotoluidine and one of paratoluidine, but it does not take place with one molecule of paraphenylenediamine and two of paratoluidine (Witt, S. C. I. 1882, 256).

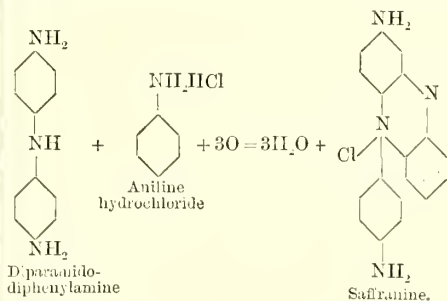
On the other hand, the other of the two molecules of monamines must have a free ortho-position in order to be capable of entering the reaction. Thus the indamine of the above formula forms saffranines with all the primary aromatic monamines of the benzene series, with the exception of one xylidine and of mesidine, of the respective formulae



because these two have no free ortho-position to be used for the formation of the azonium group (Nietzki, B. 19, 3017 and 3136).

It is also necessary that this second molecule of monamine be a primary base, whilst the one necessary for the formation of the indamine may be either primary, secondary, or tertiary, provided always that it possess a free para-position.

5. It is evident that the general process described under 4 may be modified; thus, for instance, the diparamido-derivatives of secondary bases (being the leuco-compounds of indamines) may be oxidised together with one molecule of a primary aromatic monamine, when a saffranine is the result.



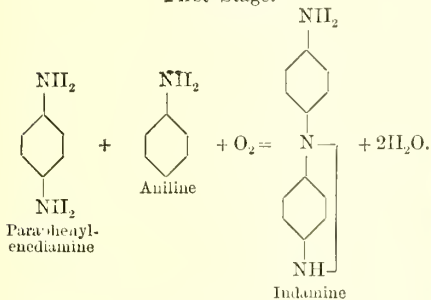
6. Another modification (Witt, B. 10, 873) consists in heating amidoazo-compounds with the hydrochlorides of aromatic monamines. This is the oldest process for the manufacture of saffranines. The mechanism of this reaction is simple. Part of amidoazo-compound being reduced, a mixture of a paradiamine and a primary monamine in molecular proportions is formed, which with the monamine added in the

4. The saffranines proper (asymmetric di-amidazonium bases) are formed by the joint oxidation of one molecule of diamine and two molecules of an aromatic monamine. In this reaction fugitive indamines are formed as intermediate products; the process thus becomes strictly analogous to the formation of toluylen-red and its congeners.

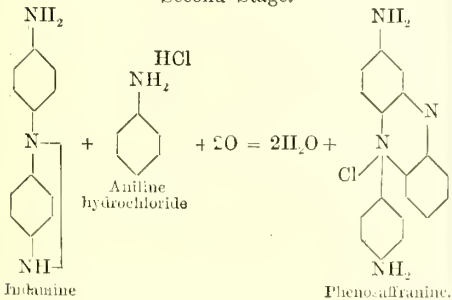
This is the process which is generally used in the manufacture of saffranines, and it will therefore be thoroughly explained.

By the joint oxidation of an aromatic paradiamine with one molecule of an aromatic monamine, an indamine is invariably formed (*v. INDAMINES*). If these indamines be oxidised in the presence of another molecule of an aromatic monamine, a saffranine is formed:

First Stage.



Second Stage.





shape of hydrochloride, is transformed into saffranine by the dehydrogenating action of the remaining part of the amidoazo-compound. It is evident that the yield must be small in this process of manufacture, and such is actually the case.

7. Certain compounds belonging to the saffranine group (mauveine &c.) are formed by the oxidation of heavy aniline alone; on continued oxidation mauveine is converted into true saffranine (Perkin, P. R. 35, 717).

The following is an account of the more important and more thoroughly investigated saffranines.

#### A. MONAMIDO- DERIVATIVES OF AZONIUM BASES.

1. **Red dyestuff**  $C_{22}H_{11}N_3Cl$ . Obtained by the action of dichloroquinonimide on phenyl- $\beta$ -naphthylamine was prepared by Nietzki and Otto (B. 21, 1598) by heating the ingredients in molecular proportion in alcoholic solution on the water-bath. The nitrate forms green needles or prisms which are soluble in water with a magenta-red colour. The hydrochloride dissolves in sulphuric acid with a red colouration, which on dilution changes through green into red.

2. **Violet colouring matter**  $C_{21}H_{20}N_3Cl$ . Prepared by Witt (B. 21, 719) by acting with 3 molecules of nitrosodimethylaniline hydrochloride in an acetic acid solution on 2 molecules of phenyl- $\beta$ -naphthylamine. This is the dimethyl-derivative of the preceding substance. The hydrochloride forms large black needles soluble in water, with a fine violet colour. The free base,  $C_{21}H_{20}N_3OH$  is liberated from the salts by caustic alkalis only. It is insoluble in water, soluble in alcohol, with a red colour and a fine orange fluorescence.

3. **Violet colouring matter**  $C_{22}H_{22}N_3Cl$ . Prepared by Witt (B. 21, 719) from paratolyl- $\beta$ -naphthylamine in exactly the same manner as the preceding substance, of which this is the next homologue. Violet, soft needles, resembling in their colour and reactions the phenyl derivative.

The above substances have been patented (Otto N. Witt, G. P. 19,224, dated Feb. 18, 1882).

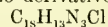
#### B. DIAMIDO- DERIVATIVES OF AZONIUM BASES.

1. **Phenosaffranine**  $C_{18}H_{13}N_3Cl$ . Discovered by Witt (exhibited in Paris in 1878 and mentioned in the catalogue of Messrs. Williams, Thomas & Dower), closely investigated by Nietzki (B. 16, 464) and by Bindschedler (B. 13, 207; 16, 865).

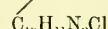
It was with this compound that the mode of formation of the saffranines and their chemical properties were definitely ascertained, chiefly by R. Nietzki, whose brilliant researches on this subject did much to clear up the chemistry of this group.

Phenosaffranine is prepared by the joint oxidation of paraphenylenediamine and aniline. The mechanism of this process has already been discussed. A dilute aqueous solution of the normal hydrochlorides of these bases is used, and their oxidation is accomplished by adding potassium or sodium bichromate or manganese dioxide in the necessary proportion to the hot solution. The blue colour of the indamine which appears

at first is immediately replaced by the red colour of the saffranine formed. A certain quantity of insoluble dark by-products is always formed, but by careful work the yield of pure saffranine may be raised to 70 per cent. of the theory. When the oxidation is finished, soda solution or milk of lime is added in order to precipitate the impurities, and the liquid is filtered. By adding a small amount of uric acid and some sodium nitrate to the filtered solution, the nitrate of the saffranine crystallises out; or the chloride may be prepared by adding common salt to the solution after acidulating it with hydrochloric acid. By repeated recrystallisation from water or alcohol, the phenosaffranine is obtained in a state of purity, in the form of magnificent green needles. The *sulphate* forms blue needles. The platinum salt  $(C_{18}H_{13}N_3Cl)_2PtCl_4$  forms insoluble shining leaflets. Phenosaffranine forms a diacetyl-derivative on boiling with acetic anhydride in the presence of dry sodium acetate. It forms two diazo-derivatives, of which the first



is rather stable and soluble in water, with a blue colouration. The other diazo- compound



is very unstable and of a green colour.

Phenosaffranine dyes wool, silk, and cotton a magnificent pink. Its aqueous solutions are red and show no fluorescence, whilst alcoholic solutions show a marked greenish-yellow fluorescence. Phenosaffranine dissolves in concentrated sulphuric acid with a green colouration which changes through blue into red on dilution, thus indicating the actual existence of the three series of salts foreshadowed by theory.

The alkyl-derivatives of phenosaffranine are interesting colouring matters, some of which have found an industrial application. They have not been prepared by introducing alkyl-groups into ready-formed saffranine, but rather by direct synthesis from suitable raw materials. Each of them exists in two isomeric modifications, according to the amido- group into which the alkyl- group has been introduced. The two amido- groups of phenosaffranine being asymmetric, and therefore not equivalent to one another, must of necessity produce different products by their being alkylated.

**$\alpha$ -Dimethylsaffranine**  $C_{20}H_{15}N_3Cl$  is produced by the simultaneous oxidation of one molecule of dimethylparaphenylenediamine with two molecules of aniline.

It is a dyestuff of a magenta-red shade. Its nitrate crystallises in green needles (Bindschedler, *l.c.*).

**$\beta$ -Dimethylsaffranine** is obtained by oxidising a mixture of one molecule of paraphenylenediamine with one molecule of aniline and one molecule of dimethylaniline. Its shade is similar to that of the preceding one; its nitrate forms brown leaflets (Nietzki, B. 19, 3017 and 3136).

The two diethyl saffranines are obtained in a similar manner. Their chlorides form green needles which dissolve in water with a violet

shade (Nietzki, B. 16, 464). These substances, and especially the  $\alpha$ -derivatives, are manufactured under the name of *fuchsia*.

**Tetramethylsafranin** (Bindschedler, *loc. cit.*) and **tetra-ethylsafranin** (Nietzki, *loc. cit.*) may be prepared by the joint oxidation of one molecule dimethyl- (or diethyl-)paraphenylenediamine with one molecule of aniline and one molecule of dimethyl- or diethylaniline. These substances have been sold under the name of *amethyst*. Their shade is a magnificent violet, with a fine crimson fluorescence. Unfortunately they are very fugitive.

**2. Tolusaffranines** (Hofmann and Geyger, B. 5, 526)  $C_{21}H_{21}N_4Cl$ . A mixture of the isomerides of this formula is the safranin of commerce. It is prepared by the oxidation of a mixture of paratoluylenediamine with the two toluidines. This mixture is obtained by treating three molecules of the orthotoluidine of commerce (which contains from 6 to 10 p.c. of paratoluidine) with two molecules of hydrochloric acid and one molecule of sodic nitrite dissolved in as little water as possible. A thick heavy oil is the result, which is merely a solution of amido-azotoluene in the excess of toluidine present. By dissolving this oil in hydrochloric acid, and reducing it with either zinc-dust or iron borings, the amido-azo-compound is split up into paratoluylenediamine and orthotoluidine; consequently the aqueous liquid produced contains the bases in the necessary proportions for the production of safranin. The rest of the treatment is exactly similar to the one described for pheno-safranin. The safranin is precipitated from the liquid by the addition of salt. By redissolving it in water, boiling with a small quantity of potassium bichromate, treating it afresh with milk of lime, and reprecipitating the filtered liquid with clean salt, the safranin is purified so as to give the brightest shades on dyeing. Safranin prepared with a toluidine rich in paratoluidine is very insoluble in cold water, and therefore generally disliked by the dyer. The presence of aniline has not the same disagreeable effect; some manufacturers therefore use the first runnings of the magenta process, which consist of aniline and orthotoluidine, and contain no paratoluidine, as a suitable raw product for the manufacture of safranin. The safranin of commerce forms a brown powder which dissolves readily in hot water. It dyes a bluish pink on textile fibres, and was chiefly used for dyeing cotton. The introduction of the so-called substantive azo-colours, derived from benzidine and its congeners, has much diminished the use of safranin.

**3. Giroflé.** A dimethylphenoxylosafranin has been produced by heating nitrosodimethylaniline hydrochloride with xylydine, and sold under the above name as a violet colouring matter of a pleasing shade.

**4. Safranisol**  $C_{18}H_{15}(OCH_3)_2N_4Cl$  is a substance which has been obtained by Nietzki by the joint oxidation of one molecule of paraphenylenediamine with two molecules of ortho-anisidine. It dyes a very beautiful yellowish-pink with a yellow fluorescence. This product has been patented (Kalle & Co., G. P. 21,22), dated Oct. 27, 1882, but owing to the high price of its production it has been unable to compete

with the eosine colours, which are perhaps still more brilliant in shade.

**5. Magdala red**  $C_{30}H_{21}N_4Cl$ . This old and very beautiful colouring matter is the safranin of the naphthalene series. It was discovered by Schiendl and first investigated by Hofmann (B. 2, 374), who, however, owing to the great difficulties of its analysis, assigned to it the erroneous formula  $C_{30}H_{21}N_4.HCl$ . After a revision of the analytical data by Julius (B. 19, 1365) its true composition was established. This substance cannot be prepared by the usual oxidation process from paranaphthylenediamine and naphthylamine because paranaphthylenediamine is at once transformed into  $\alpha$ -naphthaquinone even by the gentlest oxidising agents. Magdala red has therefore to be prepared by the old process of heating  $\alpha$ -amido-azonaphthalene with  $\alpha$ -naphthylamine acetate. The chief product of this reaction is rhodindine, the induline of the naphthalene series (*v. INDULINES*); but a small proportion (6-8 p.c.) of Magdala red is formed at the same time. This is extracted from the melt by a repeated treatment with boiling water, in which it is, although sparingly, soluble. On cooling, this solution deposits the dyestuff in the shape of gelatinous flakes. It is purified by repeated crystallisations from water. When pure, it forms a dark crystalline powder which dissolves in alcohol with a pink colour and a magnificent orange fluorescence. It is used for dyeing light pinks on silk, but is now rapidly being replaced by rhodamine (*v. TRIPHENYLMETHANE COLOURING MATTERS*). If ready-formed paranaphthylenediamine be added to the magenta-melt, the proportion of Magdala red formed is considerably increased (Otto N. Witt, G. P. 40,863, dated Dec. 30, 1886). It is thus shown that Magdala red is, after all, only a product of the joint oxidation of paranaphthylenediamine and  $\alpha$ -naphthylamine.

The salts of Magdala-red form in a perfectly pure state, if recrystallised from spirit, green needles with a metallic lustre. The chloride, sulphate, picrate, and platinum double chloride have been prepared and analysed. These salts dissolve in concentrated sulphuric acid with a blue-black colour which changes into red on dilution.

Mixed Magdala reds have been prepared either by heating amido-azonaphthalene with aromatic monamines of the benzene series (M. T. Lecco, B. 7, 1290), or by heating amidoazo-compounds of the benzene series with paranaphthylenediamine hydrochloride and aniline, toluidine, or even phenol (Otto N. Witt, G. P. 40,868). These dyestuffs resemble Magdala red in their properties.

**6. Indazine** is the commercial name of a safranin dye, which is obtained by heating the symmetrical diphenylmetaphenylenediamine (prepared by heating resorcin with aniline hydrochloride in the presence of zinc chloride) with nitrosodimethylaniline hydrochloride. Its constitution may be inferred from its analogy with the violet dyestuff prepared from nitrosodimethylaniline and  $\beta$ -naphthylphenylamine. It is a serviceable blue, of considerable intensity but little brilliancy of shade.

**7. Basle blue**  $C_{20}H_{15}N_4Cl$  is a similar blue dyestuff prepared (T. Annheim, B. 20, 1371;



Durand and Huguenin, G. P. 49,886, dated Sept. 23, 1886), by the reaction of nitrosodimethylaniline hydrochloride on the paratolynaphthylenediamine which is formed by heating Ebert and Merz's dihydroxynaphthalene with paratoluidine hydrochloride. It forms a brown crystalline powder, soluble in water, with a bluish-violet shade. In concentrated sulphuric acid it dissolves with a greenish-brown shade, which changes through green into violet on dilution.

#### SAPFRANINE DYES OF UNKNOWN CONSTITUTION.

**Mauveine**  $C_{27}H_{25}N_4Cl$ . This substance, the oldest of all the artificial colouring matters, is still manufactured in a small way, and sold under the name of rosolane. It was discovered and examined by W. H. Perkin (P. R. 35,717), who also described the mode of its production. It is prepared by oxidising heavy aniline with potassium bichromate, and extracting the mauveine formed with water or spirit from the black insoluble mass which is the chief product of the reaction. Mauveine is generally sold in the shape of a violet paste. It is insoluble in cold, sparingly soluble in hot water, easily soluble, with a fine purple shade, in spirit. Concentrated sulphuric acid dissolves it with an olive-green colouration, which changes through green and blue into purple. Mauveine holds still its own against the cheaper new violets on account of its great fastness to light and other influences. It is used for shading the white in bleached silks.

Mauveine yields on oxidation a pink dyestuff which is supposed to be identical with ordinary phenosaffranine. In our opinion this statement requires confirmation. O. N. W.

**AZO-ANTHROL COLOURS.** Anthrol, the phenol of anthracene, can easily be prepared on a large scale by the method of Liebermann and Bollert (B. 15, 226) (*v. ANTHROL*). Liebermann has used it in the preparation of a number of azo-colours, since it is of interest to know the influence which phenol, naphthol, or anthrol when used in the preparation of azo-colours has upon their shade and their stability. The colours were prepared in the usual way, viz. by mixing the solutions of the diazo-bases or their sulphonic acids with alkaline solutions of anthrol, the reactions taking place in exactly the same manner as when naphthol is used. The sulphonic acids of the colouring matters, which are either obtained by using the sulphonic acids of the bases for the preparation of the colours, or by sulphonating the insoluble colouring matters which are produced when the bases themselves are used, dye silk and wool direct, imparting to them shades similar to those obtained by naphthol colours. They vary from blood-red to a deep reddish-brown. Of course other anthracene derivatives—for instance, dioxanthracene—yield similar azo-colours (S. C. I. 1, 181).

**AZOBENZENE**  $C_{12}H_{10}N_2$ . A product of the partial reduction of nitrobenzene, obtained by Mitscherlich (A. 12, 311) by boiling an alcoholic solution of nitrobenzene with potash and distilling the product.

*Preparation.*—Azobenzene is obtained by acting with sodium-amalgam (4 to 5 p.c. of sodium) on nitrobenzene dissolved in ether containing water (Werigo, A. 135, 176; Alexejeff, J. 1864, 525; Raseneck, B. 5, -367); the pro-

duct, according to Alexejeff (J. 1867, 503) is azobenzene or azoxybenzene, according as the sodium amalgam or nitrobenzene is in excess. On the large scale azobenzene is prepared by the reduction of nitrobenzene in alcoholic solution with zinc-dust and aqueous soda. In this reaction the reduction tends to go further, and some hydrazobenzene is also obtained; this, however, is readily oxidised to azobenzene if nitrous fumes are passed into the alcoholic solution of the product (Alexejeff, J. 1867, 503). Azobenzene can also be prepared by distilling azoxybenzene (1 part) with iron filings (3 parts) (Schmidt and Schultz, B. 12, 481), and by heating nitrobenzene on a water-bath with the calculated quantity (2 mols.) of stannous chloride dissolved in excess of aqueous soda (Witt, B. 18, 2112).

*Properties.*—Azobenzene crystallises in large yellowish-red crystals belonging to the rhombic system (Alexejeff, C. S. 42, 965), m.p. at  $68^{\circ}$ , boils at  $293^{\circ}$ , and is readily soluble in alcohol and ether, insoluble in water. From benzene it crystallises with benzene of crystallisation in rhombic prisms, which lose benzene on exposure to the air. Weak reducing agents, such as ammonium sulphide or zinc-dust in alkaline solution, convert azobenzene into hydrazobenzene (Alexejeff, A. 207, 327), but benzidine is obtained when stronger reducing agents such as sulphurous acid or hydrogen iodide are employed, or the alcoholic solution is treated in the cold with stannous chloride and a little sulphuric acid (Schultz, B. 17, 464; Mentha and Heumann, B. 19, 2970). When heated with ammonium hydrogen sulphite and alcohol under pressure it is converted into benzidinesulphamic acid (Spiegel, B. 18, 1481). Azobenzene yields a mixture of mono-, di-, and tri-nitrazobenzenes when treated with fuming nitric acid (Geihardt and Laurent, A. 75, 73; Janovsky and Erb, B. 18, 1133; 19, 2157; Janovsky, M. 7, 124), whilst ordinary sulphuric acid dissolves it without alteration, although the fuming acid at  $130^{\circ}$  converts it into azobenzenemonosulphonic acid (Griess, A. 154, 203; Janovsky, M. 2, 219). The bromine derivatives of azobenzene have been examined by Werigo (A. 165, 189) and Janovsky (*l.c.*).

#### AZOBENZENE RED *v.* Azo-colouring matters.

#### AZO-BLACK or NAPHTHOL BLACK *v.* Azo-colouring matters.

#### AZO-BLUE *v.* Azo-colouring matters.

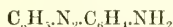
#### AZO-COCCIN *v.* Azo-colouring matters.

#### AZO-COLOURING MATTERS.

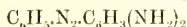
*History.*—The colouring matters of this class contain one or more azo-groups—N:N—linking together aromatic radicles. The typical parent substance from which these compounds may be regarded as being derived is azobenzene,  $C_6H_5.N:N.C_6H_5$ , which has been known since the year 1834 (Mitscherlich, A. 12, 311). The basic and acid derivatives of azobenzene are all colouring matters, the amido-derivative, amido-azobenzene, having been the first of these compounds which was prepared and introduced into commerce on anything approaching a large scale by the firm of Simpson, Maule, and Nic' o'son in 1863. This substance was prepared by the action of nitrous gas upon aniline dissolved in



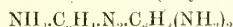
alcohol, and was known in the market by the name of 'aniline yellow,' the true constitution of the colour being at the time unknown. The introduction of the first azo-colour into commerce is thus due to the firm above mentioned, although the production of the colour itself appears to have been previously observed by Mène (C. R. 52, 311), Luthringer (Brevet d'invention, Aug. 30, 1851), and Griess (A. 1862, 121, p. 262, *note*). The first researches upon the diazo-compounds (as distinguished from azo-compounds) were published in 1858 by Griess (A. C. 106, 123), who in 1862 discovered a compound produced by the action of nitrous acid upon aniline, to which he gave the name of 'diazoamidobenzol' (A. C. 121, 257). The latter was, however, a true diazo-compound, and on comparing it with the 'aniline yellow' of commerce it was found that the two substances were isomeric, a discovery which led to the establishment of the true formula of amidoazobenzene by Martius and Griess in 1866 (Z. N.F. 2, 132). In this same year a brown dye was sent into the market by the firm of Roberts, Dale, & Co., of Manchester, and this colouring matter (known as Manchester Brown, Vesuvine, Phenylene Brown, or, more generally, Bismarck Brown) was investigated by Caro and Griess, and identified as an azo-compound (triamidoazobenzene) in 1867 (Z. N.F. 3, 278). This compound still occupies an important place in the tinctorial industries, whilst the earlier known amidoazobenzene (aniline yellow) has been completely abandoned on account of its fugitive character. In 1876 a beautifully crystalline orange colouring matter made its appearance as a commercial product under the name of 'chrysoidine,' its composition and constitution having been established by Hofmann (B. 1877, 213), who showed that it was diamidoazobenzene, being thus related on the one hand to amidoazobenzene and on the other hand to triamidoazobenzene. This colouring matter was discovered almost simultaneously by Caro and Witt, independently, in 1876, but was first introduced into commerce by the latter, the manufacture having been carried out by the firm of Williams, Thomas, & Dower, of Brentford and Fulham. The three azo-colours which thus prepared the way for the further extension of this important branch of manufacture are all amidated, and therefore basic derivatives of azobenzene, having the formulae:



Amidoazobenzene (aniline yellow)



Diamidoazobenzene (chrysoidine)



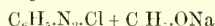
Triamidoazobenzene (Bismarck brown).

The manufacture of chrysoidine was the first industrial application of Griess's discovery of the diazo-compounds, the colouring matter in question being prepared by the action of a diazo-salt (diazobenzene chloride) upon metaphenylenediamine, and this manufacture was soon followed by the appearance of acid azo-compounds prepared by the action of diazosulphonic acids upon phenols. The typical parent substance of the acid azo-colours may be regarded

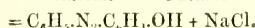
as oxyazobenzene,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , which was first prepared by Griess in 1866 (A. C. 137, 84). The general method by which the azo-colours are now prepared is an application of the reaction between diazo-salts and phenols in alkaline solution, first made known by Kekulé and Hidegh (B. 1870, 233), the first colouring matters of this class having been introduced by Witt under the name of 'Triphenolines' (C. J. 1879, 179), and simultaneously by Poirrier, of St. Denis, under the designation of 'Orange' of various brands. Since the first appearance of the acid azo-colours immense numbers of these compounds have been sent into commerce under various designations, the first patent having been taken out by Griess in 1878 (B. 1879, 12 and 143), and being quickly followed by others, which will be referred to in due order. Of the acid azo-colours described in the earlier specifications, the most successful from an industrial point of view were those manufactured by the 'Badische Anilin- und Soda-Fabrik' (B. 1879, 1364), and by Meister, Lucius, and Brüning, of Höchst (B. 1879, 144).

The next step of importance in the industrial history of the azo-colours was the introduction of *secondary azo-compounds*, containing two azo-groups. The typical compound of this class is oxy-azo-azobenzene,  $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , discovered in 1877 by Caro and Schraube (B. 1877, p. 2230). In 1879 appeared the 'Biebrich scarlet' of Nietzki (B. 1880, pp. 800, 1838), which was introduced by the firm of Kalle & Co., of Biebrich. The manufacture of this scarlet depended upon a discovery of Grässler (B. 1879, p. 396; Germ. pat. 4,186, May 12, 1878, and subsequent patents; also Krägener, B. 1882, p. 94; Germ. pat. 16,482, Nov. 14, 1879), that amidoazobenzene could, by the action of fuming sulphuric acid, be converted into a mixture of sulphonic acids capable of being diazotised. In 1881 the manufacture of a new  $\beta$ -naphthol- $\alpha$ -sulphonic acid was patented by the firm of Bayer & Co. (B. 1882, pp. 1351, 3104), from which acid were prepared a number of new secondary azo-colours, these now being met with under the name of 'Crocine Searlets.' Of late years a new series of secondary azo-compounds, derived from benzidine and its homologues, has been discovered, and these colouring matters are now extensively used, especially for cotton-dyeing. Amongst the earliest of these benzidine colours manufactured on a large scale was 'Congo red,' obtained by the action of a tetraazo-salt of this base upon  $\alpha$ -naphthylamine sulphonic acid (P. Böttiger, Germ. pat. No. 28,753; B. 1884, p. 453).

*Manufacture.*—The general method of preparing the azo-colours on a large scale depends upon the reaction between a diazo-salt, usually the chloride, and a phenol or phenolsulphonic acid in presence of an alkali, as typified by the following example:—

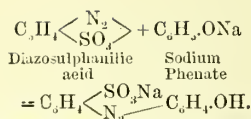


Diazobenzene-chloride      Sodium Phenate

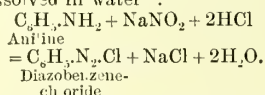


Benzeneazophenol

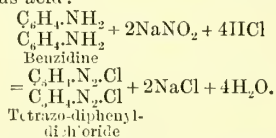
Amidosulphonic acids or amidocarboxylic acids when diazotised react in a similar manner:



In practice the diazo-salt is not isolated in the first place, but is always employed in a state of aqueous solution, the amine to be diazotised being first dissolved in dilute acid and then mixed with the calculated quantity of sodium nitrite dissolved in water<sup>1</sup>:



As diazo-salts are unstable in presence of warm water the solutions are always well cooled during the process of diazotising, the cooling being effected in large operations by floating lumps of ice in the solution. When the whole of the nitrite has been added and the diazotising operation is complete, the solution of the diazo-salt is run into the solution (also cooled) containing the calculated quantity of phenol or sulphonic acid, &c., dissolved in alkali, the amount of the latter being so adjusted as to keep the mixed solutions slightly alkaline at the end of the reaction. In most cases the colouring-matter separates out at once, or after standing for some hours; in other cases the complete precipitation of the azo-compound is promoted by the addition of common salt, and, in some few instances, the solution requires acidifying in order to precipitate the colour. The rate at which an amine becomes diazotised depends upon the state of dilution of the solution as well as the nature of the amine. It may be taken as a general rule that the simple amines, such as aniline and its homologues, the naphthylamines, &c., diazotise more rapidly than the more complex amido-derivatives, such as amidoazobenzene and its homologues. Benzidine and its homologues form tetrazo-salts when acted upon by nitrous acid:



These tetrazo-salts also combine with two molecules of a phenol, amine or sulphonic acid, and it has been observed that the combination takes place in two stages, intermediate products containing one free diazo-group being first formed (Langé, B. 1886, p. 1697). The practical application of this discovery will be seen on referring to the mixed secondary azo-compounds of this class, which are described in the detailed list of azo-colouring matters.<sup>2</sup>

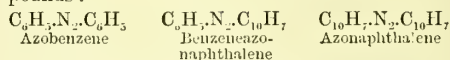
*General properties.*—The tinctorial value of the azo-colours depends upon the presence of

<sup>1</sup> Some of the diazosulphonie acids, such as diazonaphthionic acid, are insoluble in water, and are therefore employed in a state of suspension.

<sup>2</sup> According to a recent patent oxyazo-compounds can be produced by heating diazoamido-compounds with phenols according to the general reaction:

$\text{X.N}_2\text{NH.X} + \text{Y.OH} = \text{X.N}_2\text{.(Y-II).OH} + \text{X.NH}_2$  (Fischer and Michaelis, Germ. pat. 40,890, Nov. 11, 1886; B. 1887, iii, p. 754).

acid or basic radicles in the three parent compounds:



These compounds are insoluble in water and devoid of dyeing properties. The basic derivatives of azobenzene previously mentioned are soluble in dilute acids and show a regular gradation of tint, amidoazobenzene being yellow, diamidoazobenzene orange, and triamidoazobenzene reddish brown. These amidated azobenzenes are all dye-stuffs having considerable affinity for animal fibre, such as silk or wool. The hydroxy-derivatives of the parent compounds are generally soluble in alkalis and are strong colouring matters, but are not readily applicable in this form. The tinctorial value of both amidated and hydroxy-derivatives is increased when these are converted into sulphonic acids by the presence of one or more  $\text{HSO}_3$  groups in one or both radicles. The sulphonation may be effected by first forming the azo-compound and then heating the latter with sulphuric acid of appropriate strength, or, preferably, the amidosulphonic acid is diazotised and then combined with the phenol, amine or sulphonic acid in accordance with the general method of manufacture already described. The alkaline salts of such sulphonic acids are all soluble in water and are decomposed by stronger acids with the liberation of the sulphonic acid, which then combines readily with the fibre presented to it. A regular gradation of shade is shown by homologous series, thus:

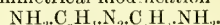
$\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{HO}\beta\text{.(HSO}_3)_2 \dots$  Benzeneazo- $\beta$ -naphtholdisulphonic acid. Orange.

$\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{HO}\beta\text{.(HSO}_3)_2 \dots$  Tolueneazo- $\beta$ -naphtholdisulphonic acid. Reddish orange.

$\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{HO}\beta\text{.(HSO}_3)_2 \dots$  Xyleneazo- $\beta$ -naphtholdisulphonic acid. Scarlet.

$\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{HO}\beta\text{.(HSO}_3)_2 \dots$  Cumeneazo- $\beta$ -naphtholdisulphonic acid. Bluish scarlet.

The shade of colour is influenced also by isomerism. Thus the unsymmetrical diamidoazobenzene  $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4\text{(NH}_2\text{)}$  is much redder than the symmetrical modification



The various isomeric naphtholsulphonic acids also give different shades of colour, and as a rule the azo-colours derived from  $\alpha$ -naphtholsulphonic acids are bluer and more soluble than those obtained from the  $\beta$ -naphtholsulphonic acids. The tinctorial power of the azo-colours appears to increase up to a certain limit with the complexity of the molecule, the secondary azo-colours derived from amidoazobenzene being more intense colouring matters than the simpler compounds containing only one  $\text{N}_2$  group. The azo-colours, both acid and basic, all dye silk and wool readily, but cannot be made to take easily upon cotton without the use of mordants. Some affinity for vegetable fibre is shown, however, by the secondary azo-colours of the Biebrich scarlet type (eroceins) and more especially by the secondary azo-compounds derived from benzidine and its homologues, these colouring matters having a distinct affinity for cotton, which makes them of special value, since they can be dyed directly on to cotton from a soap bath without the use of a mordant. The mode of ap-

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plication of these dyes to the various classes of fabrics belongs to the subject of dyeing.

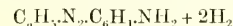
The azo-colours dissolve with characteristic colours in strong sulphuric acid, so that this reagent can be used as a rough test for these compounds. Thus the simpler primary compounds containing only benzene nuclei dissolve as a rule with an orange or red colour; secondary azo-compounds containing  $\text{HSO}_3$  groups in the benzene nucleus only, dissolve with a green colour (Biebrich scarlet,

$\text{HSO}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_3\text{H}_3(\text{HSO}_3)\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{OH}\beta$ ;  
when the  $\text{HSO}_3$  group is in the naphthalene  
nucleus the colour given by strong sulphuric  
acid is violet :—Ponceau SS,

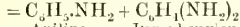
$\text{C}_6\text{H}_3\text{N}_2\cdot\text{C}_6\text{H}_4\text{N}_2\cdot\text{C}_{10}\text{H}_4(\text{HSO}_3)_2\cdot\text{OH}\beta$ ,  
and when  $\text{HSO}_3$  is present in both benzene and  
naphthalene nuclei they dissolve with a blue  
colour (crocein scarlets,

$\text{HIO}_3 \cdot \text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_7 \cdot \text{HIO}_3$  (a, HIO $\beta$ ). It must be understood, however, that the colour given by sulphuric acid is only of use in a rough preliminary examination, as the rules given above are interfered with by the circumstance that several of the primary azo-colours also dissolve with a violet or blue colour, *e.g.* Bordeaux G. fast red, &c.

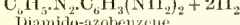
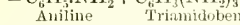
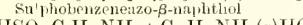
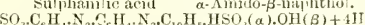
By the action of reducing agents, such as tin and hydrochloric acid, the azo-colours are reduced, and always in such a manner that the nitrogen atoms of the  $N_2$ -groups become severed and hydrogenised. This is shown by the following examples:—



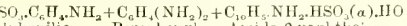
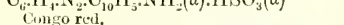
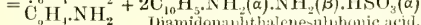
Amido-azobenzene



Aniline      Parapheny'ene-diamine,  
 $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$        $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$


$$\text{C}_6\text{H}_5\text{NH}_2 + \text{C}_6\text{H}_5(\text{N}$$

$$\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\text{OH}(\beta) + 2\text{H}_2$$

$$\text{C}_6\text{H}_4\cdot\text{NH}_2 + \text{C}_{10}\text{H}_6\cdot\text{NH}_2$$


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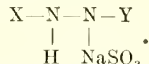
Paraphenyl-  
ene diamine      Amido- $\beta$ -naphtho:- $\alpha$ -  
sulphonic acid.
$$C_6H_4N_2 \cdot C_{10}H_5NH_2(a) \cdot HSO_3(a) + 4H_2$$
 $\cdot\text{NH}_2$  94

Benzidine, Diamidodiphenylmethane sulphonic acid.

*Identification of azo- colours.*—A process for identifying the azo- colours derived from the sulpho-acids of the naphthols and naphthylamines has been described by O. N. Witt (B. 1888, p. 3468). The method is based on the complete reduction of the colouring matter in accordance with the above principle. One gram of the substance is dissolved in 10–20 parts of hot water according to its solubility and to the solution are added 6 c.c. of a solution containing 2 grams of stannous chloride (crystals) in pure hydrochloric acid of 1.19 sp.gr. (40 grams tin salt in 100 c.c. acid). When the reduction is complete the resulting amido-naphthol or di-amidonaphthalene sulphonic acid can be identified by its properties. For the detection of azo-colours in the fibre see a paper by Lepetit (Zeit.

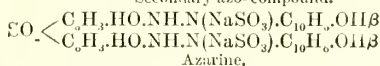
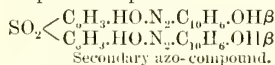
f. angew. Chem., Aug. 1888, Journ. Soc. Dyers and Colourists, vol. 4. p. 133).

*Soluble compounds formed by Azo- Colours with acid sulphites.*—Oxyazo- compounds which are insoluble in water have the property of forming easily decomposable, soluble, crystalline compounds when heated for some time in alcoholic or aqueous solution with potassium or sodium bisulphite. The compounds thus formed are yellowish in colour, soluble in water, and decomposed by steaming or by alkali, so that the colouring matter can by this means be deposited in the fibre. These water-soluble compounds have the general formula (Spiegel, Ber. 1885, p. 1479) :

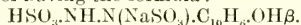


The following compounds of this class have been sent into commerce:—

**Azarine** (Meister, Lucius, and Brüning).—Diamidodioxymbenzosulphonc,  $\text{SO}_2(\text{C}_6\text{H}_3\text{HO.NH}_2)_2$ , is diazotised and the tetrazo-salt combined with  $\beta$ -naphthol in the usual way. The azo-colour, which is insoluble in water, is then converted into the bisulphite compound:



**Narceïne** (Durand and Huguenin). The bisulphite compound of sulphobenzeneazo- $\beta$ -naphthol having the formula:



The property of forming soluble compounds with bisulphites was first discovered by Prud'homme. The following patents refer to the technical application of this discovery:—Farbwerke vorm. Meister, Lucius und Brüning, Germ. pat. 29,067, December 16, 1883 (B. 1884, p. 452); Eng. pat. 5,767, December 17, 1883; Farbenfabriken vorm. F. Bayer & Co., Germ. pat. 30,080, April 19, 1884 (B. 1885, p. 11); Eng. pat. 2206, Feb. 17, 1885; Farb. vorm. Meister, Lucius und Brüning, Germ. pat. 30,598, June 1, 1884 (B. 1885, p. 89); Dreyfus, Eng. pat. 9,280, June 26, 1888, S. C. I. 1889, p. 117. This last patent relates to the formation of a bi-sulphite compound from Primuline.

*Separation of Azo- Colours by fractional precipitation.*—The isomeric naphtholsulphonic acids, which are so largely used in the manufacture of azo- colours, not only form compounds of different shades of colour with the same diazo-salt, as has already been stated above, but they differ also in the facility with which they enter into combination with such diazo-salts. Advantage is taken of this property to effect the separation of the different isomerides without previously separating the isomeric naphtholsulphonic acids. As an example of this method may be mentioned the use of diazotised benzidine (tetrazodiphenyl chloride). Thus when  $\beta$ -naphthol is sulphonated at 50–60°C., a mixture of three monosulphonic acids is produced of which only one ( $\beta$ -naphthol- $\alpha$ -sulphonic acid) is of use for the manufacture of Crocein Scarlet. The other two modifications, of which one is Schäffer's acid, are therefore removed by adding the neces-



sary quantity of diazotised benzidine to the alkaline solution of the mixed acids, when Schäffer's acid and the other modification are first precipitated as claret-red secondary azo-colours, and the  $\alpha$ -acid is left in solution in a state of purity. The latter can then be used for the preparation of crocein scarlet (Farbenfab. vorm. F. Bayer & Co., Germ. pat. 30,007, March 1, 1884; B. 1885, p. 89; Eng. pat. 8,495, May 31, 1884, S. C. I. 1885, p. 452).

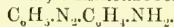
*Direct formation of Azo-Colours in the fibre.* Owing to the facility with which diazo-salts react with phenols in alkaline solution, it has been found possible to produce azo-colours directly in the fibre of the goods which have to be dyed by immersing alternately or simultaneously in a solution of naphthol and the diazo-salt, and then developing by alkali. This process is especially applicable to cotton-dyeing (T. and R. Holliday, Eng. pat. 2 757, July 6, 1889). A similar result is arrived at by using the nitrite which is necessary for diazotising in the form of an ammonium salt, so that on heating the impregnated fabric this salt is decomposed in the presence of the phenol and amine, and thus gives rise to the formation of the azo-colour (F. Grässler, Germ. pat. 14,950, November 28, 1880; Ber. 1881, p. 2079). Azo-compounds of rosaniline can be similarly introduced into fabrics by first immersing in a solution of diazotised rosaniline, and then into an alkaline solution of  $\beta$ -naphthol (Dawson, Eng. pat. 1,280, March 16, 1882). A colouring matter has recently been introduced by Brooke, Simpson, and Spiller, Limited, under the name of 'Primuline,' which can be diazotised in the fabric and then the latter, on immersion in a bath containing the phenol (naphthol or resorcinol) dissolved in alkali, develops the colour in the fibre. The same principles are applied in processes described in the following patents:—

C. Holliday, Eng. pat. 2,946, June 21, 1882; T. Holliday, Eng. pat. 2,580, February 25, 1885, and 13,790, November 12, 1885. Farbenfab. vorm. F. Bayer & Co., Germ. pat. 43,433, August 30, 1887; B. 1888, p. 557.

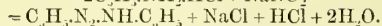
In the succeeding portion of this article it is proposed to give an account of the most important azo-colours which have been introduced into commerce. Each colour will be treated of under its commercial name; its chemical formula given, and the mode of preparation and general properties briefly described.

#### I. BASIC AZO-COMPOUNDS.

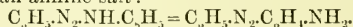
##### Aniline Yellow; Amidazo-benzene,



This compound, discovered by Mène in 1861 (J. 1861, p. 416), and introduced into commerce by Simpson, Maule, and Nicholson in 1863, is interesting as being the first azo-colour made on a manufacturing scale. It was formerly prepared by passing nitrous acid gas into an alcoholic solution of aniline. As a colouring matter it is now of no importance, but is largely used as the starting point in the manufacture of other azo-colours and of indulines. In practice this compound cannot be prepared directly by the action of one molecule of nitrous acid upon two molecules of aniline, since diazoamidobenzene is always the first product of this reaction:—



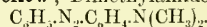
The diazo-compound is slowly converted into the isomeric aniline yellow on being allowed to stand for some time in contact with aniline and an aniline salt:—



On a large scale the diazoamidobenzene is first prepared and then dissolved in excess of aniline and a little aniline hydrochloride (2 parts diazo-compound, 1 part aniline salt, and 4 parts aniline); the mixture, after standing for a day or two at about 30°–40°C. contains nothing but amidazo-benzene, and the excess of aniline is removed by basifying with caustic soda and steam distilling. By carefully adjusting the proportions, and keeping the mixture well cooled during the addition of the nitrite, the diazo-compound can be formed directly in the presence of the excess of aniline, and need not be isolated at first. The old aniline yellow was the oxalate of the base. The free base crystallises in yellow rhombic prisms. M. p. 120°. B. p. above 300°. The hydrochloride crystallises in steel-blue needles. Base slightly soluble in hot water, readily soluble in alcohol. Yellow solution coloured red by hydrochloric acid.

*Literature.*—Mène, 1861 (see above); Dale and Caro, Eng. pat. No. 3,307, 1863; Martius and Griess, 1866, Z. 2, 132; Kekulé, 1866, *ibid.*, 2, 689; Grässler, D. P. J. 232, 192; Witt and Thomas, C. J. 1883, p. 112; Friswell and Green, C. J. 1885, p. 917; and 1886, p. 746; Stadel and Bauer, B. 1886, p. 1953.

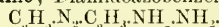
##### Butter Yellow; Dimethylamidoazobenzene,



Prepared by the action of diazobenzene chloride on dimethylaniline. Substance forms yellow leaflets of m. p. 115°; soluble in dilute hydrochloric acid with a red colour; precipitated by alkali. Soluble in strong sulphuric acid with a yellow colour becoming red on dilution.

*Literature.*—Griess, B. 1877, p. 528.

##### Chrysoidine; Diamidoazobenzene,



This colouring matter is prepared by mixing a solution of diazobenzene chloride with a solution of metaphenylene-diamine. In practice a known weight of aniline is dissolved in dilute hydrochloric acid and diazotised, the solution being diluted so as to contain 1 per cent. of diazo-salt. The necessary amount of the diamine is obtained by reducing the corresponding quantity of metadinitrobenzene<sup>1</sup> so as to obtain a 10 per cent. solution of the diamine. The colour when formed is separated by means of common salt or else directly crystallised as hydrochloride. The free base forms yellow needles; m.p. 117.5°C. Slightly soluble in water, readily in alcohol; solutions orange. The commercial product is the hydrochloride,  $\text{C}_6\text{H}_5\text{N}_2\text{HCl}$ , which forms beautiful blackish-green prisms with a metallic lustre. The strong solution of the salt solidifies on rapid cooling to a red jelly. Dissolves in strong sulphuric acid with a brownish-yellow colour. Used in combi-

<sup>1</sup> In some factories it is customary to use impure dinitrobenzene, i.e. containing a certain amount of dinitrotoluene, so that the product contains some toluylene chrysoidine formed from the metatolylene-diamine.

nation with saffranine to produce a scarlet on mordanted cotton.

*Literature.*—Hofmann, B. 1877, p. 213; Witt, *ibid.*, pp. 350 and 654; Griess, *ibid.*, p. 389.

**Azophosphines; Nitrochrysoïdines.**—These colours are prepared by the action of diazotised metanitriline and its homologues upon metaphenylene-diamine and its homologues. Thus the simplest compound of this class would have the formula:— $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\cdot\text{NH}_2\cdot\text{NH}_2$ .

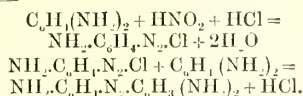
[3] [1] [2] [4]

*Literature.*—A. Leonhardt & Co., Germ. pat. 37,021, B. 1886, vol. iii., p. 803, S. C. I. 1886, p. 523.

**Bismarck Brown; Phenylene Brown; Manchester Brown; Vesuvine.**—Triamidoazobenzene,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3\cdot\text{NH}_2\cdot\text{NH}_2$ . Prepared by

[3] [1] [2] [4]

the action of nitrous acid upon metaphenylene-diamine, the reaction occurring in two stages:—



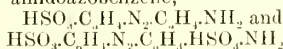
These two reactions occur simultaneously in practice, the colour being made on a large scale by reducing a known weight of dinitrobenzene with finely divided iron and a little hydrochloric acid and then boiling with water and milk of lime. The iron salts are decomposed by this treatment, and the clear solution on filtration or on being allowed to subside contains the metaphenylene-diamine. The necessary quantity of sodium nitrite and dilute hydrochloric acid are added to the cold solution, and the colour, which forms immediately, salted out and collected on filters. The commercial product consists of the hydrochloride,  $\text{C}_{12}\text{H}_{13}\text{N}_4\cdot 2\text{HCl}$ , more or less mixed with salt, and containing a certain quantity of insoluble matter which is formed as a secondary product during the reaction. The insoluble residue is a resinous substance, possibly containing the secondary azo-compound  $\text{C}_6\text{H}_3\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2$ . The free base forms yellowish-brown leaflets; m.p.  $137^\circ$ ; sparingly soluble in water, more readily in alcohol. Solutions of salts yellowish-brown, becoming redder on addition of hydrochloric acid; precipitated by alkalis. Solid colour dissolves in strong sulphuric acid with a dark-brown colour, becoming orange on dilution with water.

*Literature.*—Caro and Griess, 1867; Z. N. F. 3, p. 278.

## II. ACID AZO-COMPOUNDS.

### A. Sulphonic Acids of Amidoazo-Compounds.

**Acid Yellow; Fast Yellow;** sometimes with the brand G (*gelb*) to distinguish it from its homologue. This colouring matter is a mixture of the sodium salts of mono- and disulphonic acids of amidoazobenzene,

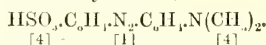


Prepared by the action of fuming sulphuric acid upon aniline yellow (3 5 parts acid to one of amidoazobenzene). Solution not precipitated by alkali; colour dissolves in strong sulphuric acid with a brownish yellow colour becoming redder on dilution. Solution gives a precipitate

with barium chloride, but not with calcium chloride. The corresponding colouring matter from amidoazotoluene is somewhat more orange in shade, and is known as **Acid Yellow R** or **Fast Yellow R**.

*Literature.*—Grüssler, Germ. pat. 4,186, B. 1879, p. 396; Germ. pat. 7,094, B. 1879, p. 2107; and Germ. pat. 9,384, B. 1880, p. 942; Nietzki, B. 1880, p. 1838; Griess, B. 1882, p. 2188; Eger, B. 1889, p. 847.

**Methyl Orange; Helianthin; Orange III.; Gold Orange; Mandarin Orange.**—Parasulphobenzene-azodimethylaniline,



[4] [1] [4]

Prepared by the action of diazotised sulphanilic acid<sup>1</sup> upon dimethylaniline, the commercial product being the ammonium or sodium salt of the sulphonic acid thus produced. Solution of colouring matter orange and not precipitated by alkali; dilute acids produce a crystalline precipitate, the crystals having a violet reflexion (the free sulphonic acid). The substance dissolves in strong sulphuric acid with a yellow colour becoming red on dilution.

*Literature.*—Griess, B. 1877, p. 528.

**Tropæ line OO; Orange No. IV.; Diphenylamine Yellow; Gold Orange; Acid Yellow D. or Fast Yellow.**—Parasulphobenzene-azodiphenylamine,  $\text{HSO}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ . Produced

[4] [1] [4]

by the action of diazotised sulphanilic acid upon diphenylamine; the market product is the potassium or sodium salt. The diphenylamine is reduced to powder and suspended in the solution containing the diazosulphonic acid, the whole being kept agitated for some hours till the reaction is complete. The colouring matter is not very readily soluble in water; the solution is yellow and when strong deposits crystals on cooling. Alkalis produce no precipitate, calcium or barium chloride gives an insoluble precipitate (Ba or Ca salt). Substance dissolves in strong sulphuric acid with a violet colour, becoming redder and giving a greyish precipitate of the free sulphonic acid on dilution. The aqueous solution of the substance is coloured red by dilute acids.

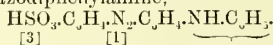
When nitrated this colour furnishes a mononitro-derivative together with a mixture of mono-, di-, and tri-nitrodiphenylamine; the resulting product is a yellow colouring matter which has been introduced into commerce under the names of **Citronine B** or **2B**, **Azo Yellow**, **Azo-flavine S** or **2**, **Jaune Indien**, **Indian Yellow**, **New Yellow**, &c. It is not to be confounded with the 'Citronine' of Brooke, Simpson, and Spiller (Meldola, C. N. 1878, vol. 37, p. 56; Witt, C. J. 1878, p. 210).

A colouring matter homologous with the preceding and prepared by the action of diazotised xylidimonomonosulphonic acid on diphenylamine was formerly in the market under the name of **LUTEOLIN**.

*Literature.*—Roussin and Poirrier, Eng. pat. 4,491, Nov. 6, 1878, Witt, B. 1879, p. 262.

<sup>1</sup> For detailed information on the manufacture of sulphanilic acid and its homologues see a paper by Mühlbacher, D. P. J. Vol. 264, pp. 181 and 238.

**Metanil Yellow; Orange MN.**—Metasulphobenzene-azodiphenylamine,



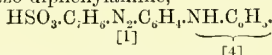
Prepared in the same manner as the preceding from metadiazobenzenesulphonic acid<sup>1</sup> and diphenylamine; market product the sodium salt. Aqueous solution orange, giving no precipitate with alkalis, becoming red and precipitating with dilute acids, and giving a difficultly soluble precipitate with barium or calcium chloride. Dissolves in strong sulphuric acid with a dull violet colour, becoming magenta red on dilution.

Introduced by the firm of K. Oehler, Offenbach on the Maine, Germany, 1882.

**Metanil Yellow S** is produced by sulphonating the preceding colouring matter.

**Metanil Orange I. and II.** are prepared by the action of diazotised meta-amidobenzenesulphonic acid on  $\alpha$  and  $\beta$ -naphthol respectively (Griess, B. 1878, p. 2197).

**Orange N; Jaune N; Curcumein.**—Sulphotoluene-azo-diphenylamine,



This colouring matter is homologous with the two preceding which it resembles in its general properties.

*Literature.*—Roussin and Poirrier, Eng. pat. 4,491, Nov. 6, 1878.

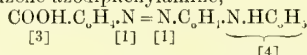
**Brilliant Yellow** (Bad. An. u. Sod. Fab.); **Acid Yellow 00.** Similar to the preceding; prepared from the sulphonic acid of commercial mixed (ortho- and para-) toluidines.

**Naphthionic Red; Archil Substitute.**—Nitrobenzene-azo- $\alpha$ -naphthylamine- $\alpha$ -sulphonic acid,  $\text{NO}_2\text{C}_6\text{H}_4\text{N}_2\text{C}_{10}\text{H}_7\text{NH}_2\text{HSO}_3$ . Prepared by the action of diazotised nitraniline upon naphthionic acid<sup>2</sup> in alkaline solution. The nitraniline is prepared by the nitration of acetanilide and subsequent hydrolysis so that it consists of a mixture of ortho- and para-nitraniline. Commercial product a paste; solution precipitated by acids and alkalis. Strong sulphuric acid dissolves colour with a magenta red becoming brownish and precipitating on dilution.

*Literature.*—Roussin and Poirrier, S. C. I., 1879, p. 292.

#### B. Carboxylic Acids of Amidoazo-Compounds.

**Jaune Solide; Fast Yellow** (for soap).—Carboxybenzene-azodiphenylamine,



Prepared by the action of metadiazobenzoic acid upon diphenylamine. Used as a yellow colouring matter fast to soap. A brown paste, difficultly soluble in water. Solution becomes reddish-violet with acids. Dissolves with a violet colour in strong sulphuric acid becoming red on dilution.

<sup>1</sup> Meta-amidobenzenesulphonic acid is prepared by sulphonating nitrobenzene and reducing the metanitrobenzenesulphonic acid thus formed.

<sup>2</sup> Naphthionic acid is manufactured on a large scale by heating  $\alpha$ -naphthylamine with 3-4 parts of strong sulphuric acid (oil of vitriol) or by heating dry naphthylamine sulphate to 180°-200°C.

*Literature.*—Soc. Anon. d. Mat. Color., Eng. pat. 4621, Sept. 1833; S. C. I. 1831, p. 319

#### C. Oxyazo-Compounds.

**Soudan Brown.**— $\alpha$ -Oxyazonaphthalene,  $\text{C}_{10}\text{H}_7\text{N}_2\text{C}_{10}\text{H}_7\text{OH}$ . Prepared by the action of diazotised  $\alpha$ -naphthylamine upon  $\alpha$ -naphthol in alkaline solution.

*Literature.*—Badische Anilin- u. Soda-Fabrik, Germ. pat. 5,411, B. 1879, p. 1364.

**Soudan G.**—Metadioxyazobenzene,  $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_5\text{OH.OH}$ .

Prepared by the action of diazobenzene chloride upon resorcinol in alkaline solution. Solution of colouring matter yellow, giving a brown precipitate with acids. Dissolves in strong sulphuric acid with a yellowish brown colour. Introduced into commerce by the 'Actiengesellschaft f. Anilinfabrikation.'

*Literature.*—Baeyer and Jäger, B. 1875, p. 151; Typke, *ibid.* 1877, p. 1576; Wallach, *ibid.* 1882, p. 24.

Benzene and Xylene-azo- $\beta$ -naphthol,  $\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{OH}(\beta)$  and  $\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{OH}(\beta)$ , have been introduced under the names of **Soudan I. and II.**

**Carminnaphtha;**  $\beta$ -naphthalene-azo- $\beta$ -naphthol. Prepared by the action of diazotised  $\beta$ -naphthylamine on  $\beta$ -naphthol in alkaline solution. Insoluble in water: soluble in strong sulphuric acid with a magenta-red colour giving a reddish-brown precipitate on dilution. Manufactured by Durand and Huguenin, Basle.

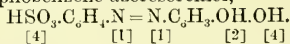
#### D. Sulphonic Acids of Oxyazo-Compounds.

##### 1. MONOSULPHONIC ACIDS.

**Tropæoline Y.**—Parasulphobenzene-azophenol,  $\text{HSO}_3\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_5\text{OH}$ . Prepared by the action of diazotised sulphanilic acid upon phenol dissolved in alkaline solution. The commercial product was the acid sodium salt; the colouring matter is no longer met with in commerce. Solution yellow, not precipitated by alkalis; precipitated by barium chloride. Solution in strong sulphuric acid brownish-yellow.

*Literature.*—Tschirvinsky, B. 1873, p. 560; Griess, *ibid.* 1878, p. 2192; Witt, *ibid.* 1879, p. 259, and C. J. 1879, p. 184.

**Tropæoline O or R; Resorcin Yellow; Chrysosin; Chrysoline; Chryséolin; Golden Yellow.**—Parasulphobenzene-azoresorcinol,



Produced by the action of diazotised sulphanilic acid upon resorcinol in alkaline solution, the commercial product being the acid sodium salt. Solution of colouring matter orange; substance dissolves in strong sulphuric acid with a yellow colour.

*Literature.*—Griess, B. 1878, p. 2195; Witt, C. J. 1879, p. 183.

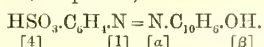
**Orange I;** **Tropæoline 000, No. 1;**  $\alpha$ -Naphthol **Orange.**—Parasulphobenzene-azo- $\alpha$ -naphthol,  $\text{HSO}_3\text{C}_6\text{H}_4\text{N}_2\text{C}_{10}\text{H}_7\text{OH}$ . Formed by the action of diazotised sulphanilic acid upon  $\alpha$ -naphthol in alkaline solution. The commercial product is the sodium salt. Solution



orange, not precipitated by alkali; the red calcium salt precipitated by calcium chloride. Dissolves in strong sulphuric acid with a violet colour, becoming orange on dilution. No longer met with in commerce.

*Literature.*—Witt, C. J. 1879, p. 184; Liebermann, B. 1881, p. 1796, and A. Ch. 1882, p. 61; Mühlhäuser, D. P. J. vol. 264, p. 181. Introduced in 1876 or 1877 by Roussin and Poirrier, of St. Denis, and about the same time by Williams, Thomas, and Dower of Brentford.

**Orange II.; Tropæoline 000, No. 2; Mandarin G;  $\beta$ -Naphthol Orange.**—Parasulphobenzene-azo- $\beta$ -naphthol,



[4] [1] [a] [β]

Prepared in the same manner as the last from  $\beta$ - instead of  $\alpha$ -naphthol. Solution orange, becoming red on addition of caustic soda. Solution in strong sulphuric acid red, becoming orange on dilution. Commercial compound, the sodium salt.

*Literature.*—Witt, C. J. 1879, p. 184; Mühlhäuser, D. P. J., vol. 264, p. 181. The industrial history is the same as that of the last colouring matter.

**Orange R; Mandarin GR**—Sulphotoluene-azo- $\beta$ -naphthol,  $\text{HSO}_3\text{C}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_4\text{OH}(\beta)$ . Homologous with the preceding, the diazotised sulphonic acid of commercial toluidine being used instead of sulphanilic acid. Commercial product the sodium salt.

**Orange 2 R.**—Sulphoxylene-azo- $\beta$ -naphthol,  $\text{HSO}_3\text{C}_6\text{H}_3\text{N}_2\text{C}_{10}\text{H}_7\text{OH}(\beta)$ .—Prepared in the same manner as the preceding from the sulphonic acid of commercial xylydine and  $\beta$ -naphthol. The commercial product is the sodium salt. Aqueous solution gives a reddish-brown precipitate with dilute acids. Dissolves with a red colour in strong sulphuric acid giving a brown precipitate on dilution.

*Literature.*—The manufacture of the two last colouring matters is described in the paper by Mühlhäuser already referred to.

**Tropæoline 0000.**—Benzeneazo- $\alpha$ -naphthol-sulphonic acid,  $\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{HSO}_3\text{OH}(\alpha)$ . This colouring matter is no longer manufactured; it was formerly prepared by the action of diazobenzene chloride upon  $\alpha$ -naphtholmonosulphonic acid in alkaline solution. An isomeric compound is in the market under the name of **Cochineal Scarlet G**, prepared from  $\alpha$ -naphtholmonosulphonic acid C. The first colouring matter dissolves in strong sulphuric acid with a magenta red and the cochineal scarlet with an orange-red colour giving a brownish precipitate on dilution.

*Literature.*—Witt, C. J. 1879, p. 184; also Hofmann, B. 1877, p. 1380. Verein Chem. Fab., Germ. pat. 26,012, 1883; S. C. I. 1884, p. 29. Also Gaess, Monit. Sci. 1884, p. 335.

**Cochineal Scarlet 2 R.**—Homologous with the preceding. Prepared by the action of diazotised toluidine on  $\alpha$ -naphtholmonosulphonic acid C. Aqueous solution reddish orange. Flaky precipitate with acids. Dissolves in strong sulphuric acid with a red colour giving red flaky precipitate on dilution. Introduced with **Cochineal Scarlet G** by the Schöllkopf Aniline and Chemical Co., Buffalo, U.S.A.

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*Literature.*—Gaess, as in preceding, and Eng. pat. 15,781, Dec. 22, 1885 (Schöll. An. Co., S. C. I. 1886, p. 164).

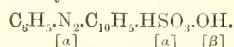
**Cochineal Scarlet 4 R.**—Homologous with preceding; prepared from diazotised xylydine and the same  $\alpha$ -naphthol-sulphonic acid. Properties similar to those of the last compound.

*Literature.*—Same as under preceding.

**Ponceau 4 GB.**—Benzeneazo- $\beta$ -naphthol-sulphonic acid,  $\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{HSO}_3\text{OH}(\beta)$ . Prepared by the action of diazobenzene chloride upon  $\beta$ -naphtholmonosulphonic acid (Schäffer's acid)<sup>1</sup> in alkaline solution.

*Literature.*—Griess, B. 1878, p. 2197.

**Crocein Orange.**—Isomeric with the preceding. Probably has the formula:



[a] [a] [β]

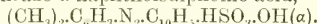
Prepared as above from Bayer's  $\beta$ -naphthol-sulphonic acid.<sup>2</sup> Commercial product the sodium salt.

**Orange GT.**—Tolueneazo- $\beta$ -naphthol-sulphonic acid,  $\text{C}_6\text{H}_5\text{N}_2\text{C}_{10}\text{H}_7\text{HSO}_3\text{OH}(\beta)$ . Homologous with the last; prepared by diazotising commercial toluidine and combining with Schäffer's  $\beta$ -naphtholmonosulphonic acid in alkaline solution. Orange aqueous solution gives an oily precipitate with acids. Dissolves in strong sulphuric acid with a magenta red giving an oily deposit on dilution. The corresponding colour from paratoluidine is **Scarlet GT**. Introduced (as sodium salt) by F. Bayer & Co., of Elberfeld.

**Scarlet GR.**—Homologous with the last; prepared from diazotised xylydine and Schäffer's acid. Dissolves in strong sulphuric acid with a red colour becoming brown and precipitating on dilution.

*Literature.*—Levinstein, B. 1880, p. 586.

**Azococcin 2 R, sometimes Xylidine Scarlet.**—Xyleneazo- $\alpha$ -naphthol-sulphonic acid,



Prepared by the action of diazoxylene chloride (commercial xylydine diazotised) upon  $\alpha$ -naphtholmonosulphonic acid in alkaline solution, the commercial product being the sodium salt. The acid is prepared by sulphonating  $\alpha$ -naphthol at a low temperature. Aqueous solution not precipitated by alkalis; when hot and concentrated deposits bronzy crystals on cooling. Dissolves in strong sulphuric acid with a reddish violet colour becoming brown and precipitating free acid on dilution.

<sup>1</sup> This acid is the chief product when  $\beta$ -naphthol is heated with not less than two parts of strong sulphuric acid to about 90° until completely sulphonated. At a lower temperature (50–60°) this and the isomeric (Bayer's) acid are formed in about equal quantity. With more acid and a higher temperature or longer time disulphonic acids are produced. (Schäffer, J. pr. 1869, p. 449; F. Bayer & Co., Germ. pat. 18,027, March 18, 1881.)

<sup>2</sup> This acid is prepared by the action of sulphuric acid upon  $\beta$ -naphthol at a moderate temperature in admixture with Schäffer's acid as above described. One part of finely powdered  $\beta$ -naphthol is gradually mixed with two parts of strong sulphuric acid (66°B.) and the mixture allowed to rise to 50°–60°C. but not beyond. For details of separation see following patents:—F. Bayer & Co., Germ. pat. No. 20,397, January 18, 1882; *ibid.* No. 26,673, June 22, 1883; *ibid.* No. 26,251, May 10, 1883, and No. 30,077, March 1, 1884, in addition to the original patent, No. 18,027, March 18, 1881, referred to in the above note. Another process for preparing this acid at a lower temperature (20°C.) is described by A. Leonhardt & Co., and Dr. R. Schulz in Germ. pat. No. 33,557, July 4, 1881.

*Literature.*—Verein Ch. Fab. Mannheim. Germ. pat. 26,012, February 27, 1883; S. C. I. 1884, p. 29.

**Fast Brown N; Acid Brown; Naphthylamine Brown.**—Sulphonaphthalene-azo- $\alpha$ -naphthol,  $\text{HSO}_3\cdot\text{C}_{10}\text{H}_6\cdot\text{N}=\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ . Prepared by the

$\begin{matrix} [\alpha] & [\alpha] & [\alpha] & [\alpha] \end{matrix}$   
action of diazotised  $\alpha$ -naphthylamine- $\alpha$ -sulphonic acid (naphthylamine acid) upon  $\alpha$ -naphthol in alkaline solution; commercial product the sodium salt. Colouring matter gives a reddish-brown solution, not changed by acids or alkalis. Dissolves in strong sulphuric acid with a reddish-violet colour.

*Literature.*—Badische Anilin- und Soda-Fabrik, Germ. pat. 5,411, March 12, 1878; B. 1879, p. 1364.

**Fast Brown 3 B.**—Sulphonaphthalene- $\beta$ -azo- $\alpha$ -naphthol,  $\text{HSO}_3\cdot\text{C}_{10}\text{H}_6\cdot\text{N}=\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ . Pre-

$\begin{matrix} [\beta] & [\beta] & [\alpha] & [\alpha] \end{matrix}$   
pared by the action of diazotised  $\beta$ -naphthylaminesulphonic acid upon  $\alpha$ -naphthol in alkaline solution. The naphthylaminesulphonic acid is prepared by heating the ammonium salt of Schäffer's  $\beta$ -naphtholmonosulphonic acid to a high temperature ( $180^\circ$ ) with ammonia:

$\text{C}_{10}\text{H}_7\cdot\text{HSO}_3\cdot\text{OH} + \text{NH}_3 = \text{C}_{10}\text{H}_6\cdot\text{HSO}_3\cdot\text{NH}_2 + \text{OH}_2$   
Aqueous solution brownish-red becoming violet with dilute acids and red with alkalis. Solution in strong sulphuric acid blue, giving reddish-violet precipitate on dilution.

*Literature.*—Brönnner, Germ. pat. 22,547, July 5, 1882, S. C. I. 1883, p. 536.

**Brilliant Double Scarlet G (Actiengesell.); Orange Red I.** Prepared from the foregoing  $\beta$ -naphthylamine sulphonic acid and  $\beta$ -naphthol. Aqueous solution gives brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour giving a brown precipitate on dilution. *Literature* as under preceding colour.

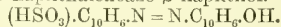
**Fast Red; Fast Red A; Roccellin; Rauracienne; Rubidine; Orseille No. 3.**—Sulphonaphthalene-azo- $\beta$ -naphthol,  $\text{HSO}_3\cdot\text{C}_{10}\text{H}_6\cdot\text{N}=\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ . Prepared by the

$\begin{matrix} [\alpha] & [\alpha] & [\alpha] & [\beta] \end{matrix}$   
action of diazotised naphthionic acid upon  $\beta$ -naphthol in alkaline solution. Commercial product the sodium salt. Substance dissolves in hot water with a reddish-brown colour; concentrated solution when rapidly cooled solidifying to a brown gelatinous mass. Soluble in strong sulphuric acid with a violet colour, becoming brown and giving a precipitate of the free acid on dilution.

*Literature.*—Badische Anilin- und Soda-Fabrik, Germ. pat. 5,411, March 12, 1878; B. 1879, p. 1364; Griess, B. 1878, p. 2199.

**Fast Red B.**—Sulphonitronaphthalene-azo- $\beta$ -naphthol,  $\text{HSO}_3\cdot\text{NO}_2\cdot\text{C}_{10}\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}(\beta)$ . Produced by the action of nitroamidonaphthalenesulphonic acid (diazotised) upon  $\beta$ -naphthol in alkaline solution. Introduced by the Badische Anilin- und Soda-Fabrik as the sodium salt. Colour more violet in shade than the preceding.

**Acid Ponceau (Durand and Huguenin).** Sulpho- $\beta$ -naphthalene-azo- $\beta$ -naphthol.



$\begin{matrix} [\gamma] & [\beta] & [\alpha] & [\beta] \end{matrix}$

Prepared by sulphonating  $\beta$ -naphthylamine, diazotising the mixed isomeric sulpho-acids

<sup>1</sup> A mixture of this with  $\beta$ -naphthol orange was formerly sold under the name of 'Rouge Français.'

and combining with  $\beta$ -naphthol in alkaline solution. Aqueous solution gives a brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour becoming brown and precipitating on dilution.

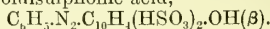
**Ponceau 3 G; Scarlet 3 G.**—Sulphoanisole-azo- $\beta$ -naphthol,  $\text{HSO}_3\cdot\text{OCH}_3\cdot\text{C}_6\text{H}_3\cdot\text{N}=\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ .

$\begin{matrix} [\alpha] & [\beta] \end{matrix}$   
Produced by the action of diazotised amidoanisole-sulphonic acid upon  $\beta$ -naphthol in alkaline solution. Commercial product the sodium salt. The anisidinesulphonic acid is prepared by sulphonating anisidine or by nitrating and reducing anisolsulphonic acid.

*Literature.*—Badische Anilin- und Soda-Fabrik, Germ. pat. 12,451, January 3, 1879. B. 1881, p. 552; and S. C. I. 1881, p. 121.

## 2. DISULPHONIC ACIDS.

**Orange G; Orange Yellow.**—Benzeneazo- $\beta$ -naphtholdisulphonic acid,



Produced by the action of diazobenzene chloride upon  $\beta$ -naphtholdisulphonic acid (G salt)<sup>1</sup> in alkaline solution. Commercial product the sodium salt. Solution not precipitated by alkali; a crystalline calcium salt formed on adding calcium chloride (orange leaflets). Dissolves in strong sulphuric acid with an orange colour, undergoing no change on dilution.

*Literature.*—Meister, Lucius, and Brüning, Germ. pat. 3,229, April 24, 1878; B. 1879, p. 144.

**Ponceau 2 G (Meister, Lucius, and Brüning).** Isomeric with the preceding. Prepared by the action of diazobenzene chloride upon  $\beta$ -naphtholdisulphonic acid (R salt). Properties similar to those of the preceding compound; colour slightly redder in shade.

*Literature* as above.

**Ponceau GT.**—Tolueneazo- $\beta$ -naphtholdisulphonic acid. Homologous with preceding; prepared by the action of diazotised toluidine on the G salt. The isomeric compound from the R salt is **Ponceau RT**.

*Literature*, see preceding compound.

**Ponceau R (Bad. An. u. Sod. Fab.); Ponceau 2 R (Meister, Luc., and Brü. and Actiengesell.), Scarlet G; Xylidine Red.**—Xyleneazo- $\beta$ -naphtholdisulphonic acid,  $\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6(\text{HSO}_3)_2\cdot\text{OH}(\beta)$ . Produced by the action of diazotised commercial xylidine (para- and metaxylidine) upon  $\beta$ -naphtholdisulphonic acid (R salt). Properties similar to those of Orange G. Colour a distinct scarlet; aqueous solution not precipitated by alkali; an amorphous precipitate by calcium or barium chloride. Soluble with a red colour in strong sulphuric acid, becoming brown and precipitating on dilution.

<sup>1</sup> When  $\beta$ -naphthol is heated with three times its weight of strong sulphuric acid to  $100^\circ$ – $110^\circ$  for twelve hours a mixture of two isomeric disulphonic acids is produced, the one giving a sodium salt (G salt) which furnishes yellow shades of azo-colours than the other (R salt). For details concerning the manufacture and separation of these acids see the following patents:—Meister, Lucius, and Brüning, Germ. pat. 3,229, April 24, 1878; Leipziger, Anilinfabrik, Germ. pat. 33,916, April 19, 1884; S. C. I. 1885, p. 339. Other patents relating to naphtholdisulphonic acids are:—L. Gans and M. Hoffmann, Eng. pat. 816, January 5, 1884; S. C. I. 1884, p. 367, and 1885, p. 742; Farbfabrik vorm. Brönnner, Germ. pat. 26,938, July 21, 1883; H. Baum, Germ. pat. 4,199, September 13, 1883, Monit. Scien. 1883, p. 1121; L. Gans & Co. Germ. pat. 35,019, January 15, 1884. See also Griess, B. 1880, p. 128<sup>1</sup>.

*Literature*, see above. The isomeric compound from the G salt is yellower in shade, and is known as **Ponceau G**.

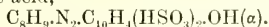
**Ponceau 3 R**; **Cumidine Red** (Meister, Luc. and Brü.).—Cumeneazo- $\beta$ -naphtholdisulphonic acid,  $C_9H_7.N_2.C_{10}H_7(HSO_3)_2.OH(\beta)$ . Produced by the action of diazocumene chloride (from  $\psi$ -cumidine)<sup>1</sup> upon the R salt. Properties as above; colour of a redder shade than the last.

*Literature*, see above.

**Ponceau 3 R** (Meister, Luc., and Brü.).—Ethyl-dimethylbenzeneazo- $\beta$ -naphtholdisulphonic acid,  $C_2H_5.(CH_3)_2.C_6H_2.N_2.C_{10}H_7(HSO_3)_2.OH(\beta)$ . Prepared by the action of diazotised ethyl-xylidine<sup>2</sup> upon the R salt.

*Literature*, see above.

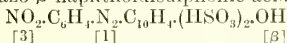
**Wool Scarlet R**.—Xyleneazo- $\alpha$ -naphtholdisulphonic acid,



Prepared by the action of diazotised xylidine upon the disulphonic acid in the usual manner. Commercial product the sodium salt; reddish solution becomes violet on addition of acid. Sulphuric acid solution red, unaltered on dilution. Introduced by the Schöllkopf Aniline Co., Buffalo, U.S.A. Eng. pat. 15,775, Dec. 22, 1885; S. C. I. 1886, p. 164.

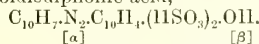
**Buffalo Rubin**.—The corresponding colour from diazotised  $\alpha$ -naphthylamine and the same  $\alpha$ -naphtholdisulphonic acid. References as in preceding. Another colouring matter of the same formula and probably isomeric has been introduced by the Farb. vorm. F. Bayer & Co. It is known as *Naphthorubin*, and is prepared by the action of diazotised  $\alpha$ -naphthylamine on the  $\alpha$ -naphtholdisulphonic acid prepared according to the patent of Gericke and Rudolf (Eng. pat. 15,716, Dec. 21, 1885).

**Orange No. 3** (not Helianthin).—Metanitrobenzeneazo- $\beta$ -naphtholdisulphonic acid,



Prepared by the action of diazotised metanitriline upon R salt; commercial product the sodium salt. Orange aqueous solution gives an orange precipitate with acids. Dissolves in strong sulphuric acid with an orange yellow colour giving a precipitate on dilution which dissolves in more water. Colouring matter but seldom met with now. Introduced by Roussin and Poirrier. Germ. pat. 6,715, Nov. 19, 1878; D. P. J. 1879, p. 423.

**Bordeaux G**; **Claret G**.— $\alpha$ -Naphthaleneazo- $\beta$ -naphtholdisulphonic acid,



Prepared by combining  $\alpha$ -diazonaphthalene chloride with sodium  $\beta$ -naphtholdisulphonate, G salt. Commercial product the sodium salt. Solution gives a flocculent precipitate with barium or calcium chloride. Substance dissolves in strong sulphuric acid with an indigo-blue colour.

*Literature*.—Meister, Lucius, and Brüning, Germ. pat. 3,229, April 24, 1878. B. 1879, p. 144.

<sup>1</sup> This cumidine is manufactured by heating xylidine hydrochloride and methyl alcohol to 280°-300° in autoclaves. Actiengesell. f. Anilinfab., Germ. pat. 22,265, July 1, 1882.

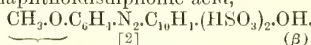
<sup>2</sup> Prepared like cumidine, by heating xylidine hydrochloride and ethyl alcohol to a high temperature in autoclaves.

**Bordeaux R** or **B**; **Claret Red**.—Isomeric with the last, the R salt being used instead of the G salt. Colour somewhat bluer in shade but otherwise similar in its properties to the preceding.

*Literature* as in the last.

**Crystal Ponceau 6 R**; **New Coccin R**.— $\alpha$ -Naphthaleneazo- $\beta$ -naphtholdisulphonic acid ( $\gamma$ -modification).<sup>1</sup> Produced by the action of diazotised  $\alpha$ -naphthylamine upon  $\beta$ -naphthol- $\gamma$ -disulphonic acid in alkaline solution. Commercial product the sodium salt. Introduced by Casella & Co.

**Anisole Red**; **Anisidine Ponceau**.—Anisoil-azo- $\beta$ -naphtholdisulphonic acid,

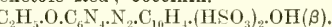


[1]

Prepared by the action of diazotised anisidine upon  $\beta$ -naphtholdisulphonic acid (R salt) in alkaline solution. Commercial product the sodium salt; colouring matter now not often met with. Anisole red appears at one time to have been prepared from a monosulphonic acid of  $\beta$ -naphthol. Substance gives a red solution with strong sulphuric acid. An isomeric anisole red was formerly made from diazotised anisidine-sulphonic acid and  $\beta$ -naphtholmonosulphonic acid (Schäffer's).

*Literature*.—Griess, Eng. pat. 4,726, Nov. 20, 1878; Meister, Lucius, and Brüning, Germ. pat. 7,217, Dec. 3, 1878; B. 1879, p. 2108; Badische Anilin- und Soda-Fabrik, Germ. pat. 12,451, Jan. 3, 1879, B. 1881, p. 552. S. C. I. 1881, p. 121.

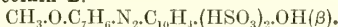
**Phenetole Red**; **Coccin**.—



Homologous with the last; prepared from amido-phenetol instead of anisidine. Substance dissolves in strong sulphuric acid with a red colour.

*Literature* as in the preceding. No longer in the market.

**Coccin B**.—

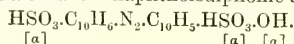


Prepared by diazotising the amido-derivative of methyl-anisole (amidocresol-methyl-ether), and combining with the R salt of  $\beta$ -naphtholdisulphonic acid in presence of alkali. Commercial product the sodium salt; solution not precipitated by alkali; a brown precipitate with barium chloride and a red precipitate gradually formed on addition of calcium chloride. Soluble in strong sulphuric acid with a magenta-red colour becoming more orange on dilution.

*Literature*.—Meister, Lucius, and Brüning, Germ. pat. 7,217, Dec. 3, 1878; B. 1879, p. 2108.

**Cresol Red**.—The higher homologue of the last compound; prepared from the ethyl-ether of amido-cresol. Introduced by the Badische Co.

**Azorubin S** (Actiengesell.); **Fast Red C** (Badische Co.); **Carmoisin** (Bayer). Sulpho- $\alpha$ -naphthaleneazo- $\sigma$ -naphtholsulphonic acid,



[a]

[a]

[a]

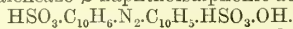
<sup>1</sup> This acid is obtained by sulphonating Bayer's monosulphonic acid under certain special conditions, or by the diazo-reaction from  $\beta$ -naphthylaminedisulphonic acid. See Eng. pat. 816, Jan. 5, 1884, by Leo Gans and M. Hoffmann, S. C. I. 1884, p. 567, and 1885, p. 742. Also Germ. pat. 35,019, Jan. 15, 1884, Frankfurter Anilinfarbenfabrik, Gans & Co.



Prepared by the action of diazotised naphthionic acid upon  $\alpha$ -naphtholmonosulphonic acid (Nev. and Win.) in presence of alkali; commercial product the sodium salt. Solution gives a red crystalline precipitate with calcium chloride; substance dissolves in strong sulphuric acid with a bluish-violet colour becoming red on dilution.

*Literature.*—Verein Chem. Fab., Germ. pat. 26,012, Feb. 27, 1883, S. C. I. 1884, p. 29.

**Fast Red E** (Badische Co.).—Sulpho- $\alpha$ -naphthaleneazo- $\beta$ -naphtholsulphonic acid,



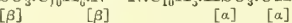
Isomeric with the preceding; prepared from diazotised naphthionic acid and Schäffer's  $\beta$ -naphtholmonosulphonic acid. Aqueous solution claret red; not precipitated by acids, dissolves in strong sulphuric acid with a violet colour becoming red on dilution.

*Literature.*—Badische Co., Germ. pat. 5,411, March 12, 1878 (v. list of patents).

**Crocein Scarlet 3 BX** (Bayer).—Isomeric with the last; prepared from diazotised naphthionic acid and Bayer's  $\beta$ -naphthol- $\alpha$ -sulphonic acid. Commercial product the sodium salt; hot solution (concentrated) gives a crystalline magnesium salt on adding magnesium sulphate and allowing to cool; solution in strong sulphuric acid reddish violet becoming yellowish red on dilution.

*Literature.*—Farb. vorm. F. Bayer & Co., Germ. pat. 20,402, March 30, 1882 (v. list of patents).

**Double Scarlet Extra S**; **Brilliant Scarlet Extra** (Actiengesell.).—Isomeric with the last; prepared from diazotised  $\beta$ -naphthylaminesulphonic acid (Brönner's), and  $\alpha$ -naphtholsulphonic acid:— $\text{HSO}_3\text{C}_{10}\text{H}_6\text{N}=\text{N}\cdot\text{C}_{10}\text{H}_7\text{HSO}_3\text{OH}.$



Aqueous solution gives yellowish brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour becoming yellower on dilution.

*Literature.*—Farb. vorm. Brönner, Germ. pat. 22,547, July 5, 1882, S. C. I. 1883, p. 536.

**Pyrotin** (Dahl & Co.). Isomeric with the preceding. Prepared from  $\beta$ -naphthylamine-monosulphonic acid (Dahl's) and  $\alpha$ -naphthol- $\alpha$ -monosulphonic acid. Aqueous solution yellowish red becoming bluer with acid. Dissolves with a magenta red in strong sulphuric acid, remaining red on dilution.

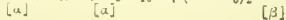
*Literature.*—Dahl & Co., Germ. pat. 29,084, March 2, 1884 (v. list of patents).

### 3. TRISULPHONIC ACIDS.

**Atlas Scarlet No. 3** (Brooke, Simpson, and Spiller). Sulphoxylenaeazo- $\beta$ -naphtholdisulphonic acid,  $\text{HSO}_3\text{C}_{10}\text{H}_6\text{N}_2\text{C}_{10}\text{H}_7(\text{HSO}_3)_2\text{OH}(\beta).$  Commercial product formerly the sodium salt; the substance is no longer manufactured. Prepared by the action of diazotised xylydinesulphonic acid upon  $\beta$ -naphtholdisulphonic acid in presence of alkali.

*Literature.*—Meldola, Eng. pat. 1864, May 10, 1879; B. 1880, p. 992; C. N., vol. 42, p. 60.

**New Coccin** (Actiengesell.); **Brilliant Ponceau** (Casella); **Cochineal Red A** (Bad. Co.).—Sulpho- $\alpha$ -naphthaleneazo- $\beta$ -naphtholdisulphonic acid,  $\text{HSO}_3\text{C}_{10}\text{H}_6\text{N}_2\text{C}_{10}\text{H}_7(\text{HSO}_3)_2\text{OH}.$  The



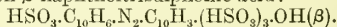
commercial product is the sodium salt, and is prepared by the action of diazotised naphthionic acid upon  $\beta$ -naphtholdisulphonic acid (G salt) in the usual way. Aqueous solution red, not precipitated by acids. Dissolves in strong sulphuric acid with a red colour becoming yellowish red on dilution.

*Literature.*—Badische Anilin- und Soda-Fabrik, Germ. pat. 5,411, March 12, 1878, B. 1879, p. 1364. Meister, Lucius, and Brünig, Germ. pat. 3,229, April 24, 1878, B. 1879, p. 144.

**Fast Red D** (Badische Co.); **Bordeaux S** (Actiengesell.).—**Amaranth** (Meister, Luc, and Brül.).—Isomeric with the preceding; being prepared from diazotised naphthionic acid and R salt. Literature as in the preceding.

**Ponceau 4 R** (Casella).—Isomeric with the preceding; prepared from diazotised naphthionic acid and  $\beta$ -naphthol- $\gamma$ -disulphonic acid (see note to Crystal Ponceau 6 R, p. 243).

**Ponceau 6 R** (Meister, Lucius, and Brünig); Prepared by the action of diazotised naphthionic acid on  $\beta$ -naphtholtrisulphonic acid:—

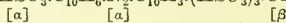
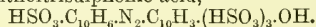


Aqueous solution red; unchanged by dilute acids. Strong sulphuric acid gives a violet solution becoming red on dilution.

*Literature.*—Meister, Lucius, and Brünig, Germ. pat. 22,038, May 26, 1882 (v. list of Patents).

### 4. TETRASULPHONIC ACIDS.

**Ponceau 6 R** (Meister, Lucius, and Brünig); **Amaranth** (Casella). Sulpho- $\alpha$ -naphthaleneazo- $\beta$ -naphtholtrisulphonic acid,<sup>1</sup>

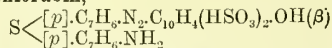


Commercial product (sodium salt) prepared by the action of diazotised naphthionic acid upon  $\beta$ -naphtholtrisulphonic acid in presence of alkali.

*Literature.*—Meister, Lucius, and Brünig, Germ. pat. 22,038, May 27, 1882; S. C. I. 1883, p. 243.

### 5. AZOTHIO-COMPOUNDS.

**Thiorubin,**



Thio-*p*-toluidine is diazotised and combined with  $\beta$ -naphtholdisulphonic acid (R salt). Aqueous solution magenta red giving yellowish-brown precipitate with mineral acids. Sulphuric acid solution red giving yellowish-brown precipitate on dilution.

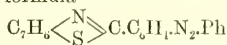
*Literature.*—Merz and Weith, B. 1871, 393; Dahl & Co., Germ. pat. 34,299, June 25, 1885, and 35,790, Nov. 7, 1885 (v. list of patents under these dates).

**Primuline,**  $(p)\text{CH}_3\cdot\text{C}_6\text{H}_3\text{<} \begin{matrix} \text{N} \\ \text{S} \end{matrix} \text{C}_6\text{H}_7\text{NH}_2.$

Prepared by heating 2 mols. of *p*-toluidine with 4 atomic proportions of sulphur till the evolution of hydrogen sulphide ceases. The commercial product is prepared by sulphonating the thio-base so as to form amidobenzenyl-*p-m*-amidothiocresolmonosulphonic acid. The latter is a

<sup>1</sup> This acid is prepared by the extreme sulphonation of  $\beta$ -naphthol by means of fuming sulphuric acid. For details see the above patent of Meister, Lucius, and Brünig; also Eng. pat. 706, February 9, 1883, by Ivan Leviinstein; B. 1884, p. 159.

yellow dye capable of taking on to cotton, and by the action of nitrous acid can be diazotised in the fibre. The diazo-compound can then be made to combine with phenols by passing the fabric through a solution of the phenol in alkali, thus forming 'ingrain' colours of great fastness in the fibre (*v. p.* 238 of this article). The azo-colours from the unsulphonated thio-base have the general formula—



where Ph represents the phenolic residue.

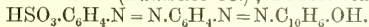
*Literature.*—A. G. Green, S. C. I. 1888, 179; Proc. C. S. 1889, 46, and C. J. Trans. 1889, p. 227; Jacobson, B. 1889, 330; Gattermann, B. 1889, 422; Pfützing and Gattermann, B. 1889, 1063.

### E. Secondary Azo-Compounds.<sup>1</sup>

**Soudan III.**— $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4\text{N}_2\text{C}_{10}\text{H}_7\text{OH}(\beta)$ . Prepared by the action of diazotised amidoazobenzene on  $\beta$ -naphthol. Insoluble in water; dissolves in strong sulphuric acid with a green colour, becoming blue, and finally red and precipitating on dilution.

*Literature.*—Nietzki, B. 1880, p. 1838.

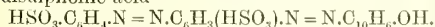
**Fast Scarlet** (Badische Co.); **Double Scarlet**.



Prepared by the action of diazotised amidoazobenzene sulphonie acid<sup>2</sup> upon  $\beta$ -naphthol dissolved in alkali.

*Literature.*—Caro and Schraube, B. 1877, p. 2230 and 1880, p. 803.

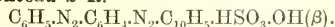
**Biebrich Scarlet**; **Ponceau 3 R** or **3 RB**; **Azobenzene Red**; **New Red**; **Imperial Scarlet**.—A mixture of the preceding colour and the disulphonic acid



Prepared from diazotised Acid Yellow (which see) and  $\beta$ -naphthol dissolved in caustic soda. Commercial product, the sodium salt; solution not precipitated by alkali; a brown flocculent precipitate by dilute acids. Dissolves in strong sulphuric acid with a green colour becoming first blue and finally brown and precipitating on dilution.

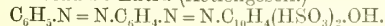
*Literature.*—See under Acid Yellow, and the following: Nietzki, B. 1880, p. 800 and 1838; W. v. Miller, *ibid.* p. 542; Krügener, Germ. pat. 16,482, Nov. 14, 1879; B. 1882, p. 94.

#### **Ponceau 2 R.**—



Two isomers in the market prepared by the action of diazotised amidoazobenzene on Schäffer's or Bayer's  $\beta$ -naphtholsulphonic acid. (See Vignan and Boasson, Ber. 1880, p. 1060.)

#### **Ponceau SS Extra** (Actiengesell.)



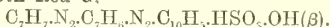
Prepared by the action of diazotised amidoazobenzene upon  $\beta$ -naphtholdisulphonic acid (R salt) in alkaline solution; commercial product,

<sup>1</sup> It will be sufficient to give the chemical formulæ of these secondary azo-compounds without giving their names in full.

<sup>2</sup> Prepared by the action of diazosulphanilic acid on aniline. Griess, B. 1876, p. 630, and 1882, p. 2183. This method does not appear to be of any technical value, as the yield is too small (Griess). The direct sulphonation of amidoazobenzene, according to the original patent of Griessler (No. 4186, May 12, 1878), gives a mixture of the mono- and di-sulphonic acids of amidoazobenzene (see under Acid Yellow).

the sodium salt. Dissolves in strong sulphuric acid with a violet colour, becoming redder on dilution. (Krügener's pat., under Biebrich Scarlet.)

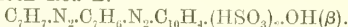
#### **Cloth Red G.**—



Produced by the action of diazotised amidoazotoluene on  $\beta$ -naphtholsulphonic acid (Schäffer's). Dissolves in water with a red-brown colour giving a similarly coloured precipitate on addition of acid. Dissolves with a blue colour in strong sulphuric acid giving a brownish-red precipitate on dilution.

*Literature.*—Oehler (Krügener), Germ. pat. 16,482, Nov. 14, 1879, and Farb. vorm. F. Bayer & Co., Eng. pat. 5,003, 1879.

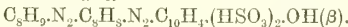
#### **Cloth Red B.**—



Prepared by the action of diazotised amidoazotoluene upon  $\beta$ -naphtholdisulphonic acid (R salt). Aqueous solution red becoming brownish on addition of hydrochloric acid. Dissolves in strong sulphuric acid with a blue colour giving a brownish-red precipitate on dilution.

*Literature* as under preceding colour.

#### **Archil Red A.**



Prepared by the action of diazotised amidoazoxylene on  $\beta$ -naphtholdisulphonic acid (R salt) in presence of alkali. Introduced (1880) by the Badische Co. Soluble in water with a Bordeaux-red colour; reddish-brown flocculent precipitate on adding dilute acid. Solution in strong sulphuric acid dark blue giving reddish-brown precipitate on dilution.

*Literature.*—Schuncke, Am. pat. 246,221, 1880. Meister, Lucius, and Brüning, Germ. pat. 22,010, Sept. 2, 1882, S. C. I. 1883, p. 243.

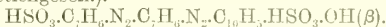
**Crocein Scarlet 3 B** (Bayer); **Ponceau 4 RB** (Actiengesell.).



Produced by the action of diazotised amidoazobenzene sulphonie acid on  $\beta$ -naphthol- $\alpha$ -sulphonic acid (Bayer's); commercial product, the sodium salt. Solution not precipitated by alkali; a red precipitate produced by barium chloride becoming dark violet and crystalline on boiling. Dissolves in strong sulphuric acid with a deep-blue colour, becoming violet and then red on dilution.

*Literature.*—Farb. vorm. F. Bayer & Co., Germ. pat. 18,027, March 18, 1881, S. C. I. 1882, p. 224, and Germ. pat. 30,077, March 1, 1884, B. 1885, p. 89.

**Crocein Scarlet 7 B** (Bayer); **Ponceau 6 RB** (Actiengesell.).



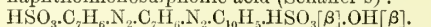
Prepared by the action of diazotised amidoazotoluenesulphonic acid on  $\beta$ -naphtholsulphonic acid (Bayer's) in presence of alkali. Resembles the preceding in general properties; gives a crystalline magnesium salt on adding magnesium sulphate to hot concentrated solution and allowing to cool. Dissolves with a blue colour in strong sulphuric acid, becoming red on dilution.

*Literature* as under preceding.

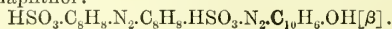
**Orseillon 2 B** (Bayer).—Prepared by the action of diazotised amidoazotoluenesulphonic acid on  $\alpha$ -naphtholsulphonic acid (Nev. and Win.). Dissolves with a blue colour in strong sulphuric acid, becoming red on dilution.

*Literature.*—Verein. chem. Fab., Germ. pat. 26,012, Feb. 27, 1883 (v. list of patents).

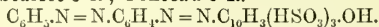
**Bordeaux G** (Bayer).—Prepared by the action of diazotised amidoazotoluenemonosulphonic on  $\beta$ -naphtholmonosulphonic acid (Schäffer's):



**Bordeaux B** (Bayer).—Diazotised amidoazoxylendisulphonic acid is combined with  $\beta$ -naphthol:



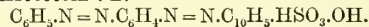
**Scarlet 5 R; Ponceau 5 R.**—



Prepared by the action of diazotised amidoazobenzene on  $\beta$ -naphtholtrisulphonic acid in alkaline solution; commercial product the sodium salt.

*Literature.*—Farb. vorm. Meister, Lucius, and Brining, Germ. pat. 22,038, May 27, 1882; S. C. I. 1883, p. 243.

**Azococcin 7 B.**—

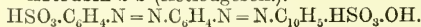


Prepared by the action of diazotised amidoazobenzene on  $\alpha$ -naphtholmonosulphonic acid (Nev. and Win.) in alkaline solution. Dissolves in strong sulphuric acid with a violet colour, giving a brownish-red precipitate on dilution. Introduced by the 'Verein Chem. Fab.,' Germ. pat. 26,012, February 27, 1883; S. C. I. 1884, p. 29.

**Croceïn B.**—The disulphonic acid corresponding to the preceding: produced by the action of diazotised amidoazobenzene on  $\alpha$ -naphtholdisulphonic acid in the usual way (Schöllkopf An. Co., Eng. pat. 15,775, Dec. 22, 1885; S. C. I. 1886, p. 164).

The homologue from diazotised amidoazotoluene is known as **Croceïn 3 B** of the same firm.

**Azorubin 2 S** (Actiegesell.).—



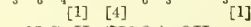
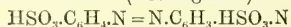
Produced by the action of diazotised amidoazobenzene on  $\alpha$ -naphtholmonosulphonic acid (Nev. and Win.) in alkaline solution. Dissolves in strong sulphuric acid with a green colour becoming blue and finally brownish-yellow on dilution. Reference as under Azococcin.

**Brilliant Croceïn M.**— $\text{C}_6\text{H}_7\cdot\text{N} = \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}$

$= \text{N}\cdot\text{C}_{10}\text{H}_7(\text{HSO}_3)_2\cdot\text{OH}$ . Prepared by the action of

diazotised amidoazobenzene on  $\beta$ -naphthol- $\gamma$ -disulphonic acid. Dissolves in strong sulphuric acid with a reddish violet becoming first bluer and then red on dilution. Manufactured by L. Casella & Co. (See note to Crystal Ponceau 6 R, p. 243.)

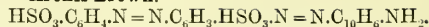
**Ponceau S Extra** (Actiegesell.).—



Prepared by the action of diazotised amidoazobenzene on  $\beta$ -naphtholdisulphonic acid (R salt) in the usual way. Commercial product the sodium salt; dissolves in strong sulphuric acid with a blue colour, becoming redder on dilution.

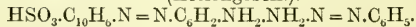
*Literature.*—W. v. Miller, B. 1880, pp. 542 and 803; Nietzki, *ibid.* pp. 980 and 1838.

**Archil Brown.**—



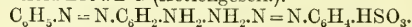
Prepared by the action of diazotised amidoazobenzene on  $\alpha$ -naphthylamine.

**Acid Brown R** (Actiegesell.).—



Prepared by the action of diazotised naphthionic acid on chrysoidine. Aqueous solution brown giving brown precipitate with acids. Dissolves in strong sulphuric acid with a dirty olive brown becoming first reddish and then brown and precipitating on dilution. Introduced by the 'Actiegesellschaft f. Anilinfab.,' Germ. pat. 22,714, November 8, 1882; S. C. I. 1884, p. 28.

**Acid Brown G** (Actiegesell.).—



Prepared by the action of diazobenzene chloride on chrysoidinesulphonic acid. The latter is prepared by the action of diazotised sulphanilic acid on metaphenylenediamine. The substance dissolves in strong sulphuric acid with a red-brown colour becoming yellowish on dilution.

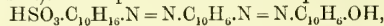
*Literature* as in preceding.

**Resorcin Brown.**—



Diazoxylene chloride is combined with Resorcin Yellow (p. 240). Commercial product the sodium salt: aqueous solution gives a brown precipitate with acids. Dissolves in strong sulphuric acid with a brown colour. (Actiegesell. Germ. pat. 18,861, Aug. 9, 1881, Die Chem. Ind. 1882, p. 291.)

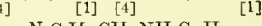
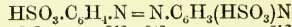
**Blue Black B** (Badische Co.); **Azo Black** (Meister, Lucius, and Brining).—The sulphonic acid of  $\beta$ -naphthylamine (Badische acid, Germ. pat. 20,760, 1881) is diazotised and combined with  $\alpha$ -naphthylamine and the product diazotised and combined with  $\beta$ -naphtholdisulphonic acid (R salt). The product has the composition:—



Aqueous solution gives a bluish precipitate with acids and caustic soda. Solution in strong sulphuric acid bluish-green becoming blue, and finally precipitating on dilution.

*Literature.*—Bad. An. u. Sod. Fab. as above (v. list of patents).

**Wool Black.**—



Prepared by the action of diazotised amidoazonaphthalenedisulphonic acid on paratolyl- $\beta$ -naphthylamine.<sup>1</sup> Aqueous solution gives a violet precipitate with acids. Dissolves with a blue colour in strong sulphuric acid giving a brown precipitate on dilution, and decomposing on boiling with the formation of Acid Yellow and tolunaphthazine. (Actiegesell. f. Anilinfab., Germ. pat. 38425, March 31, 1886. Eng. pat. 9754, July 28, 1886; S. C. I. 1887, p. 523.)

**Azo-Black or Naphthol Black** introduced by the firm of L. Casella & Co., is prepared by

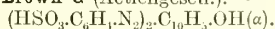
<sup>1</sup> Prepared by heating  $\beta$ -naphthol with paratoluidine and dry calcium chloride:

$\text{C}_{10}\text{H}_7\cdot\text{OH} + \text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{HCl} = \text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{C}_6\text{H}_4 + \text{OH}_2 + \text{HCl}$   
(E. Friedländer, Ber. 1883, p. 2078).



the action of diazotised amidoazonaphthalene-disulphonic acid on  $\beta$ -naphtholdisulphonic acid (R salt). Aqueous solution dark violet, becoming dark blue with acid or alkali; barium and calcium chloride give a precipitate. Dissolves in strong sulphuric acid with a dark green colour, becoming blue on dilution. (Eng. pat. 9,214, July 31, 1885; S. C. I. 1886, p. 427.)

#### Fast Brown G (Actiengesell.).—

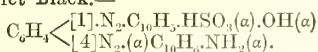


Prepared by the action of diazotised sulphanilic acid (2 mols) on  $\alpha$ -naphthol (1 mol). Aqueous solution red-brown; violet precipitate with dilute acid. Strong sulphuric acid solution violet, becoming yellowish-brown on dilution.

#### Fast Brown (Meister, Lucius, and Brüning).

Homologous with the preceding. Prepared by the action of two molecules of diazotised xylinedimonomosulphonic acid on one molecule of  $\alpha$ -naphthol. Aqueous solution brown; violet precipitate with dilute acids. Soluble in strong sulphuric acid with a violet colour, becoming red on dilution.

#### Violet Black.—

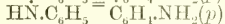
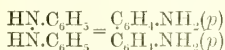


Paranitracetanilide is reduced by mild reducing agents (iron and acetic acid) and the amido-acetanilide diazotised and combined with 1 mol. of  $\alpha$ -naphtholmonosulphonic acid (Nev. and Win.). The acetyl-group is then removed by heating with acid or alkali, the amido-compound again diazotised and combined with 1 mol. of  $\alpha$ -naphthylamine. Aqueous solution brownish-red giving violet precipitate with mineral acids and reddish-violet colouration with acetic acid or with caustic soda. Blue solution in strong sulphuric acid giving violet precipitate on dilution.

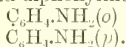
*Literature.*—Nietzki, B. 1884, pp. 343 and 1350. Also Bad. An. und Sod. Fab., Germ. pat. 42,814, April 19, 1887 (v. list under Feb. 22, 1887).

#### F. Secondary azo-compounds derived from benzidine and its homologues, anisidine and its homologues, &c.

Benzidine or paradiamidodiphenyl is prepared from azobenzene<sup>1</sup> by reduction in the presence of acids, the hydrazobenzene,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ , which is formed as an intermediate product, being converted by molecular transposition into benzidine:

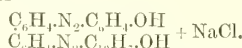
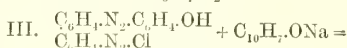
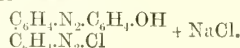
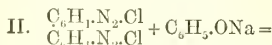
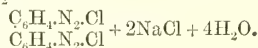
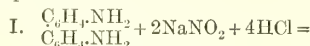


At the same time a small quantity of the isomeric compound diphenylene is formed:



By the reduction (in presence of acid) of azo-toluene, azoxylene, &c., the homologues of benzidine are produced. The amido-groups in these bases are capable of being diazotised and the tetrazo-salts thus formed combine first with one and then with a second molecule of a phenol, amine, phenolsulphonic acid, or amidosulphonic acid, so that mixed products can by this means

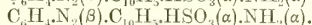
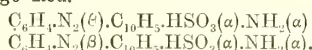
be obtained as shown by the following typical example:—



The literature relating to benzidine will be found in the following papers:—Zinin, J. pr. 1815, vol. 30, p. 93; Hofmann, J. f. 1863, p. 424; Schultz, A. 1874, vol. 174, p. 227. A paper on the colouring matters of this group with dyed patterns by G. Hurst will be found in the 'Journ. of the Soc. of Dyers and Colourists,' Feb. 25, 1888, p. 14. A paper on the azo-colours from isomeric tolidines and diamidodixyls by Nöling and Stricker will be found in B. 1888, p. 3138.

The chief azo-colours of this group which are met with in commerce are the following

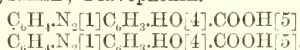
#### Congo Red.—



Prepared by the action of diazotised benzidine (one molecular proportion) on naphthionic acid (two molecules). The tetrazodiphenyldichloride is added to the well-cooled solution of sodium naphthionate, and then sodium acetate added; the reaction requires several hours for its completion, owing to the formation of the intermediate product already referred to.<sup>1</sup> The commercial product is the sodium salt; the red aqueous solution becomes blue on addition of dilute acids; substance dissolves in strong sulphuric acid with a slaty blue, giving a bluish precipitate on dilution.

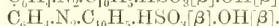
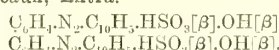
*Literature.*—P. Böttiger, Germ. pat. 28,753, February 27, 1884, B. 1884, p. 453; Eng. pat. 4,415, March 5, 1884; Witt, B. 1886, p. 1719.

#### Chrysamin; Flavophenin.—



Prepared by the action of diazotised benzidine (one molecule) on two molecules of salicylic acid in alkaline solution. Commercial product the sodium salt; used for dyeing cotton goods yellow directly from a soap bath. Aqueous solution orange, becoming redder on addition of caustic soda; orange flocculent precipitate, with dilute sulphuric acid. Soluble in strong sulphuric acid, with a magenta-red colour becoming orange and precipitating on dilution. Introduced by the 'Farbenfabriken vorm. F. Bayer & Co.,' Germ. pat. 31658, June 14, 1884; S. C. I. 1885, p. 400. The homologue from tetrazoditolyl is Chrysamin R.

#### Bordeaux, Extra.—



Prepared from tetrazoditolyl and two molecules of  $\beta$ -naphtholmonosulphonic acid (from Badische

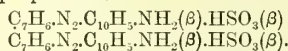
<sup>1</sup> Azobenzene is best prepared by reducing nitrobenzene in alcoholic solution with zinc-dust and caustic soda (Alexandri, Z. 1868, N. F. vol. 4, p. 107).

<sup>1</sup> Martius, B. 1886, p. 1755; Lange, *ibid.* p. 1697.

amido-acid). Aqueous solution gives violet precipitate with acids (excepting acetic). Violet solution in strong sulphuric acid precipitating on dilution.

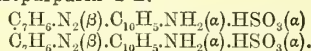
*Literature.*—Farb. vorm. F. Bayer & Co., Germ. pat. 30,077, March 1, 1884 (*v. list of patents under March 18, 1881*).

#### Benzopurpurin B.—



Prepared by the action of diazotised tolidine (one molecule) on  $\beta$ -naphthylaminesulphonic acid (two molecules) in presence of alkali. The  $\beta$ -naphthylaminesulphonic acid is the so-called  $\beta$ -modification obtained (mixed with the  $\alpha$  and  $\gamma$ -isomerides) by heating  $\beta$ -naphthylamine with 3 parts of sulphuric acid (96 to 97 p.c. of  $\text{H}_2\text{SO}_4$ ) to 100–105°C. for 6 hours (Badische Co., Germ. pat. 20,760, November 17, 1881; Dahl & Co., Germ. pat. 29,084, March 2, 1884, and 32,276, November 14, 1884), or by heating Schæffer's  $\beta$ -naphtholsulphonic acid with ammonia (Brönner, Germ. pat. 22,547, July 5, 1882—see this article under 'Fast Brown 3 B'). Aqueous solution, orange red; unchanged by caustic soda; a brownish-red precipitate by dilute sulphuric acid. Dissolves in strong sulphuric acid with a blue colour, giving a brown precipitate on dilution. Benzopurpurin B is made by the Farb. vorm. F. Bayer & Co.; Eng. pat. 3,803, March 14, 1885; also Bayer and Duisberg, Ber. 1887, p. 1428. (See also list of patents under March 17, 1885.)

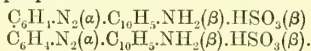
#### Benzopurpurin 4 B.—



Prepared by the action of diazotised tolidine (one molecule) on naphthionic acid (two molecules). Homologous with Congo red and isomeric with the last. Aqueous solution orange red, giving a red precipitate with excess of caustic potash; blue precipitate with hydrochloric acid; dissolves in strong sulphuric acid with a pure blue colour. Introduced by the Farb. vorm. F. Bayer & Co.; references as in the preceding.<sup>1</sup>

**Benzopurpurin 6 B.**—Prepared as above from tetrazoditoly and Laurent's naphthylaminemonosulphonic acid. The latter is prepared by sulphonating  $\alpha$ -nitronaphthalene with fuming sulphuric acid and reducing the nitrosulphonic acid. Colouring matter very similar in properties to the preceding. References as above.

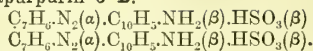
#### Deltapurpurin G.—



Isomeric with Congo red; prepared by the action of diazotised benzidine on  $\beta$ -naphthylamine- $\delta$ -sulphonic acid, the latter being prepared by heating  $\beta$ -naphthylamine sulphate with 5-6 parts of strong sulphuric acid (66° B.) to 150° for 1½ hour. The  $\alpha$ - and  $\gamma$ -monosulphonic acids of  $\beta$ -naphthylamine are also said to be transformed into the  $\delta$ -modification by this treatment. Colouring matter no longer in the market. (Farb. vorm. Bayer & Co., Eng. pat. 5846, April 29, 1886; also Bayer and Duisberg, Ber. 1887, p. 1426.)

<sup>1</sup> According to Knecht (Journ. Soc. Dyers and Colourists, 1886, p. 112) Benzopurpurin 4 B is produced by the action of diazotised diamidodiphenetol on  $\beta$ -naphthylaminemonosulphonic acid.

#### Deltapurpurin 5 B.—

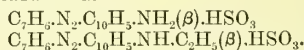


Prepared from tetrazoditoly and 1 mol. of the  $\delta$ -acid + 1 mol. of the Brönner acid. Owing to the  $\delta$ -acid being a mixture of isomerides the colouring matter contains also Benzopurpurin B and Deltapurpurin 7 B (see below). Aqueous solution orange giving a brown colouration with acetic acid, and a brown precipitate with hydrochloric acid. Red precipitate with caustic soda. Solution in strong sulphuric acid blue giving a brown precipitate on dilution. (Bayer & Co.; Germ. pat. 42,021, April 14, 1886. Also Bayer and Duisberg, B. 1887, p. 1426, and Schultz, *ibid.* p. 3158.)

**Diamine Red 3 B.**—Isomeric with the preceding. Prepared from diazotised tolidine and  $\beta$ -naphthylamine-F-sulphonic acid. The latter is prepared by fusing the sodium salt of  $\alpha$ -naphthalenedisulphonic acid (Ebert and Merz, B. 1876, p. 612), with four times its weight of 50 per cent. caustic soda at 200°C. until dioxynaphthalene begins to be formed.  $\beta$ -naphthol-F-sulphonic acid is formed, and this on being heated with ammonia in an autoclave furnishes the corresponding amido-acid. The colouring matter is precipitated from its aqueous solution by acetic acid, and forms an insoluble calcium salt. Red precipitate with caustic soda. Solution in strong sulphuric acid blue giving brown precipitate on dilution. (L. Casella & Co., Eng. pat. 12,908, Oct. 9, 1886; S. C. I. 1887, p. 725. Also Weinberg, B. 1887, p. 2906.)

**Deltapurpurin 7 B.**—Probably identical with the preceding, being prepared from the purified  $\delta$ -acid and tetrazoditoly. References as under Deltapurpurin 5 B.

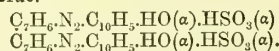
#### Roseazurin G.—



Prepared by the action of tetrazoditoly on one molecule of  $\beta$ -naphthylaminemonosulphonic acid and then on one molecule of the  $\delta$ -methyl-derivative of the same sulphonic acid. Aqueous solution red giving violet precipitate with mineral acids. Not precipitated by acetic acid. Blue solution in strong sulphuric acid giving violet precipitate on dilution. The corresponding colour from one molecule of tetrazoditoly and two molecules of methyl- $\beta$ -naphthylaminemonosulphonic acid is Roseazurin B. (Farb. vorm. F. Bayer & Co., Eng. pat. 17,083, December 30, 1886; S. C. I. 1888, p. 31.)

A colouring matter prepared by the action of one molecule of tetrazodanisole on two molecules of  $\beta$ -naphthylaminemonosulphonic acid (Brönner's) was formerly in the market under the name of ROSEAZURIN.

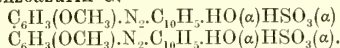
#### Azo-Blue.—



Prepared by the action of diazotised tolidine on  $\alpha$ -naphtholmonosulphonic acid. Commercial product the sodium salt. Aqueous solution of colouring-matter violet, becoming crimson on addition of caustic soda; restored to violet by dilute sulphuric acid. Dissolves in strong sulphuric acid with a pure blue colour giving violet precipitate on dilution. (Farb. vorm. F. Bayer

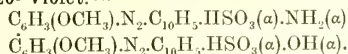
& Co., Germ. pat. 35,341, August 1, 1885; S. C. I. 1886, p. 427.)

#### Benzozaurin G.—



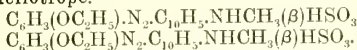
Prepared by the action of diazotised diamidodiansoil on  $\alpha$ -naphtholmonosulphonic acid. The dianisole derivative is prepared by reducing orthonitroanisole in alcoholic solution with zinc-dust and caustic soda so as to form an azo-dianisole which gives the desired compound on reduction in presence of acid, just in the same manner as nitrobenzene gives azobenzene, hydrazobenzene, and benzidine. Aqueous solution bluish-violet, becoming red on addition of caustic potash; dark-violet precipitate with dilute hydrochloric acid. Dissolves in strong sulphuric acid with a blue colour giving violet precipitate on dilution (Farb. vorm. F. Bayer & Co., Eng. pat. 14,424, November 24, 1885, S. C. I. 1886, p. 428). The homologue from diazotised diamidodiphenetol is **Benzozaurin B**.

#### Azo-Violet.—



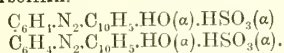
Diazotised anisidine (one mol.) is combined with one mol. of naphthionic acid, and then with one mol. of  $\alpha$ -naphthol- $\alpha$ -sulphonic acid (Nev. and Win.). Aqueous solution reddish-violet, giving blue precipitate with mineral acids and bluish-violet colouration with acetic acid. Solution turned magenta by caustic soda. Dissolves with a blue colour in strong sulphuric acid, giving a blue precipitate on dilution (Farb. vorm. F. Bayer & Co., Germ. pat. 40,247, Feb. 9, 1886; v. List of Patents).

#### Heliotrope.—



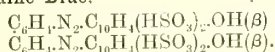
Prepared by the action of diazotised diamidodiansoil on methyl- $\beta$ -naphthylaminemonosulphonic acid. Aqueous solution red, giving violet precipitate with mineral acids and reddish-violet colouration, with acetic acid. Dissolves with a blue colour in strong sulphuric acid, giving violet precipitate on dilution (Farb. vorm. F. Bayer & Co., Germ. pat. 43,204, June 8, 1887; v. List of Patents under December 30, 1886).

#### Azo-orseillin.—



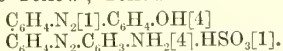
Prepared by the action of diazotised benzidine on  $\alpha$ -naphtholsulphonic acid. Commercial product the sodium salt; a paste dissolving in strong sulphuric acid with a blue colour, becoming violet on dilution (Verein. chem. Fab., Germ. pat. 26,012, February 27, 1883; v. List of Patents).

#### Benzidine Blue.—



Prepared from diazotised benzidine and  $\beta$ -naphtholdisulphonic acid (R salt). Not met with in commerce at present time (Schultz, B. 1884, p. 461).

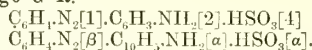
#### Congo Yellow; Yellow Paste.—



Prepared by acting with diazotised benzidine on one molecule of phenol and then combining the

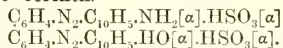
resulting product with one molecule of sulph-anilic acid. Dissolves in strong sulphuric acid with a reddish-yellow colour (Actiengesell. f. Anilinfab., Germ. pat. 39,096, August 29, 1885; also Eng. pat. 15,296, December 12, 1885; S. C. I. 1886, p. 595).

#### Congo G R.—



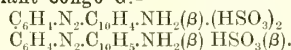
Prepared by the action of diazotised benzidine on meta-amidobenzenesulphonic acid (one molecule), and then on one molecule of naphthionic acid. Aqueous solution brownish-red, giving blue precipitate with hydrochloric and violet colouration with acetic acid. Solution in strong sulphuric acid blue, giving blue precipitate on dilution (Actiengesell. Germ. pat. 40,954, January 28, 1886; v. List of Patents).

#### Congo Corinth.—



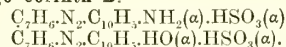
Prepared as above from tetrazodiphenyl,  $\alpha$ -naphthylaminesulphonic acid and  $\alpha$ -naphtholsulphonic acid. Aqueous solution red; violet precipitate with hydrochloric acid and colouration with acetic acid. Solution in strong sulphuric acid blue, giving violet precipitate on dilution (Actiengesell. Germ. pat. 39,096, August 29, 1885; v. List of Patents under December 12, 1885).

#### Brilliant Congo G.—



From diazotised benzidine,  $\beta$ -naphthylaminedisulphonic acid and  $\beta$ -naphthylaminemonosulphonic acid (Brønner's). Aqueous solution gives a brownish-violet precipitate with hydrochloric acid. Solution in strong sulphuric acid blue, giving violet precipitate on dilution (Actiengesell. Germ. pat. 41,095, March 30, 1887; v. List of Patents).

#### Congo Corinth B.—



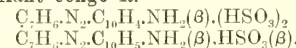
From diazotised tolidine, naphthionic acid and  $\alpha$ -naphtholsulphonic acid. Aqueous solution magenta red, giving violet precipitate with mineral acids. Blue solution in strong sulphuric acid; violet precipitate on dilution (Actiengesell. Germ. pat. 39,096, August 29, 1885; v. List of Patents under December 12, 1885).

#### Congo 4 R.—



From diazotised tolidine, resorcinol and naphthionic acid. Aqueous solution brownish-red, violet precipitate with mineral acids, brown precipitate with acetic acid. Solution in strong sulphuric acid blue giving violet precipitate on dilution (Actiengesell. Germ. pat. 39,096, Aug. 29, 1885; v. List under Dec. 12, 1885).

#### Brilliant Congo R.—

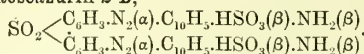


From diazotised tolidine,  $\beta$ -naphthylaminedisulphonic acid and  $\beta$ -naphthylaminemonosulphonic acid (Brønner's). Aqueous solution brownish-red, giving a similarly coloured precipitate with mineral acids. Solution becomes bluer with acetic acid. Orange precipitate with caustic soda. Blue solution in strong sulphuric



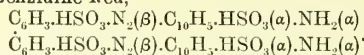
acid, giving dark-brown precipitate on dilution (Actiengesell. Germ. pat. 41,095, March 30, 1887; v. List of Patents).

#### Roseazurin 2 B.



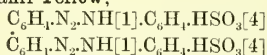
Benzidinesulphone (1 mol.) is diazotised and combined with 2 mols. of  $\beta$ -naphthylaminemonosulphonic acid (Brönner's). Aqueous solution magenta red giving a brownish-red precipitate with acids and a blue precipitate with caustic soda. Sulphuric acid solution reddish-violet, giving a brownish-red precipitate on dilution (Farb. vorm. F. Bayer & Co. v. List under Jan. 20, 1885).

#### Benzidine Red,



Prepared by diazotising the disulphonic acid of benzidine and combining the tetrazo-compound with 2 mols. of naphthionic acid. Aqueous solution magenta red giving blue precipitate with mineral acids, and violet precipitate with acetic acid. Caustic soda gives a red precipitate with concentrated solution. Blue solution in strong sulphuric acid giving blue precipitate on dilution. Colour no longer in market (Farb. vorm. F. Bayer & Co. v. List of Patents under Dec. 5, 1883, and Jan. 9, 1884).

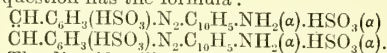
#### Sulphanil Yellow,



A diazoamido-compound produced by the action of diazotised benzidine (1 mol.) on 2 mols. of sulphanilic acid. Colour no longer in the market (v. List of Patents under Nov. 20, 1884).

### G. AZO-COMPOUNDS DERIVED FROM STILBENE.

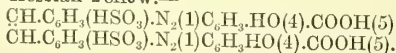
**Hessian Purple P.**—This colouring matter is one of a group of secondary azo-compounds prepared by the action of diazotised diamidostilbenedisulphonic acid on phenols, amines, sulphonic and carboxylic acids. The compound in question has the formula:



The diamidostilbenedisulphonic acid is prepared by heating the sulphonic acid of paranitrotoluene with caustic alkali and then reducing the dinitrostilbenedisulphonic acid thus produced.<sup>1</sup> The colouring matter is produced by diazotising the diamidosulphonic acid (1 mol.) and combining the tetrazo compound with naphthionic acid (2 mols.). Aqueous solution orange, becoming blue with acids, and violet with alkali. Red solution in strong sulphuric acid, giving reddish-violet precipitate on dilution.

*Literature.*—A. Leonhardt & Co., Germ. pat. 38,735, January 29, 1886; B. 1887, p. 183; v. List of Patents under January 29 and December 14, 1886.

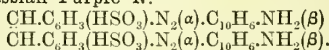
#### Hessian Yellow.—



<sup>1</sup> For an account of the azo-colours from orthodiamidostilbene see paper by C. A. Bischoff, B. 1883, p. 2073.

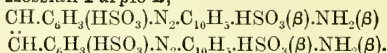
Prepared like the last from diazotised diamidostilbenedisulphonic acid and salicylic acid. Aqueous solution ochreous, giving blackish precipitate with mineral acids. Solution reddened by caustic soda. Reddish-violet solution in strong sulphuric acid, giving blackish precipitate on dilution. References as in preceding.

#### Hessian Purple N.—



From diamidostilbenedisulphonic acid diazotised and  $\beta$ -naphthylamine. Aqueous solution red, giving bluish-black precipitate with mineral acids, and violet-black precipitate with acetic acid. Red colouration or precipitate with caustic soda. Blue solution in strong sulphuric acid, giving bluish-black precipitate on dilution. References as in preceding.

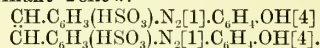
#### Hessian Purple B,



Prepared by the action of tetrazostilbenedisulphonic acid (1 mol.) on 2 mols. of  $\beta$ -naphthylaminemonosulphonic acid (Brönner's). Aqueous solution red giving brownish-black precipitate with mineral acids. Reddish-violet precipitate with caustic soda. Violet solution in strong sulphuric acid giving brown precipitate on dilution. References as in preceding.

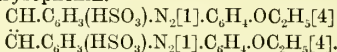
**Hessian Purple D.** Isomeric with the preceding. Prepared from the above tetrazodisulphonic acid and Dahl's  $\beta$ -naphthylaminemonosulphonic acid (v. List of Patents under March 2, 1884). Aqueous solution orange giving brown precipitate with mineral acids, and becoming redder with caustic soda. Violet solution in strong sulphuric acid becoming brown on dilution. References as in preceding.

#### Brilliant Yellow.—



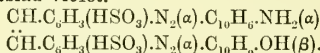
From the same diazotised disulphonic acid and phenol. Aqueous solution orange, giving violet precipitate with mineral acids. Dissolves with a reddish-violet in strong sulphuric acid, giving a violet precipitate on dilution. References as in preceding.

#### Chrysophenin.—



Prepared by ethylating the preceding colouring matter. Aqueous solution orange, giving brown precipitate with mineral acids. Dissolves with a reddish-violet colour in strong sulphuric acid, giving blue precipitate on dilution. References as in preceding.

#### Hessian violet.—



Prepared by combining 1 mol. of diazotised diamidostilbene disulphonic acid with 1 mol. and  $\alpha$ -naphthylamine, and then with 1 mol. of  $\beta$ -naphthol. Aqueous solution reddish-violet, becoming bluer with acetic acid, and giving a blue precipitate with mineral acids. Solution in strong sulphuric acid blue, giving a violet precipitate on dilution. Reference as in preceding.

## PATENTS RELATING TO AZO-COLOURING MATTERS.

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
1878. March 12.	Amido-, Bromamido-, Chlor-amido-, and Iodamido-phenol and homologues and their sulphonic acids. Amidosalicyclic acid and its sulphonic acid.	Phenol and its homologues, resorcinol, orcinol, the naphthols and sulphonic acids, dioxynaphthalene and sulphonic acid.	J. P. Griess, Germ. pat. 3224, B. 1879, p. 143.
March 12	$\alpha$ -Naphthylamine and its sulphonic acid (naphthionic acid)	$\alpha$ and $\beta$ -naphthol and their sulphonic acids.	Badische Anilin- und Soda-Fabrik, Germ. pat. 5411, B. 1879, p. 1364.
April 24.	Xylidine and homologues; the naphthylamines, &c.	$\beta$ -Naphtholdisulphonic acids.	Meister, Lucius, and Brüning, Germ. pat. 3229, B. 1879, p. 144.
May 12 .	Sulphonic acids of amido-azo-benzene and homologues.	[Used as an acid yellow.]	F. Grässler, Germ. pat. 4186, B. 1879, p. 396.
Nov. 6 .	Ortho- and paratoluidine sulphonic acids.	The naphthols, phenol-sulphonic acid, diphenylamine, phenylene diamine, dinaphthylamine, &c.	Roussin and Poirrier, Eng. pat. 4491.
Nov. 19 .	Nitraniline and homologues, nitronaphthylamine.	Phenol and sulphonic acid, the naphthols and sulphonic acids, resorcinol, diphenylamine and naphthionic acid.	Roussin and Poirrier, Germ. pat. 6715, D. P. J. 1879, p. 423.
Nov. 20 .	Amidated phenol-ethers such as amidoanisoil and homologues, amido-naphthol-ethers, &c.	Phenols and sulphonic acids.	J. P. Griess, Eng. pat. 4726.
Dec. 3 .	Amido-phenols and their ethers, amido-naphthols.	$\beta$ -Naphtholdisulphonic acids.	Meister, Lucius, and Brüning, Germ. pat. 7217, B. 1879, p. 2108; addition to pat. 3229 above.
1879. Jan. 3.	Amidated phenol and naphthol ethers and their sulphonic acids.	Naphthols and sulphonic acids.	Badische Anilin- und Soda-Fabrik, Germ. pat. 12451, B. 1881, p. 552.
Feb. 13 .	Sulphanilic acid . . .	Aniline . . .	F. Grässler, Germ. pat. 7094, B. 1879, p. 2107; addition to pat. 4186 above.
Feb. 15 .	Aniline and homologues .	$\alpha$ - and $\beta$ -naphtholsulphonic acids.	I. Levinstein, Eng. pat. 623, B. 1880, 586.
May 10 .	Sulphanilic acid and homologues, naphthylamine sulphonic acid.	Di- and tri-sulphonic acids of naphthols.	R. Meldola, Eng. pat. 1864, B. 1880, 692; C. N., vol. 42, p. 60.
Sept. 28 .	Sulphonic acids of amidoazo-benzene. Sulphonation by sulphuric anhydride and chlorosulphuric acid.	[Used as an acid yellow.]	F. Grässler, Germ. pat. 9384, B. 1880, 942; addition to pat. 4186 above.
Nov. 14 .	Amidoazobenzene and homologues and their sulphonic acids.	Phenols, naphthols, dioxynaphthalene and sulphonic acids.	R. Krügener, Germ. pat. 16482, B. 1882, p. 94.
Dec. 3 .	Sulphonic acids of amido-azobenzene.	Resorcinol, orcinol, and their sulphonic acids.	F. Grässler, Germ. pat. 16483, B. 1882, p. 95.
1880. March 18.	$\alpha$ -Naphthylaminedisulphonic acid.	Phenols and their ethers and sulphonic acids. Amines and their sulphonic acids.	E. ter Meer & Co., Germ. pat. 10797; G. Schultz's 'Chemie des Steinkohlentheers,' 1st ed. p. 242.
June 7 .	$\beta$ -Naphthylamine and sulphonic acids. $\alpha$ - or $\beta$ -naphthylamine sulphonic acids.	$\beta$ -Naphthol and sulphonic acids. Methyl, phenyl, tolyl, xylol and naphthyl- $\alpha$ - or $\beta$ -naphthylamine.	Badische Anilin- und Soda-Fabrik, Germ. pat. 7007; G. Schultz's 'Chem. des Steinkohlentheers,' 1st ed. p. 241.
Dec. 10 .	Aniline and homologues, naphthylamine.	Sulphonic acid of salicylic acid.	Ch. Fabrik auf Actien vorm. E. Schering, Germ. pat. 15117, B. 1881, p. 2134.

PATENTS RELATING TO AZO- COLOURING MATTERS—*continued.*

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
1881. Jan. 22.	Amidated methyl and ethyl ethers of aromatic acids (benzoic and cinnamic).	$\beta$ -Naphtholdisulphonic acids.	Farbwerke vorm. Meister, Lucius und Brüning, Germ. pat. 15250, B. 1881, p. 2434; S. C. I. 1882, p. 24.
Feb. 18	Amidated methyl and dimethylnaphthalene. Sulphanilic and naphthionic acids, acid yellow and aromatic bases.	$\beta$ -Naphthol and sulphonic acids. Methyl and dimethyl- $\beta$ -naphthol and sulphonic acids.	Actiengesell. f. Anilinfabrikation, Germ. pat. 25649, B. 1881, p. 2604.
March 18	Aniline and homologues, the naphthylamines, amidoazobenzene and sulphonic acids.	$\beta$ -Naphthol - $\alpha$ -sulphonic acid.	Farbenfabriken vorm. F. Bayer & Co., Germ. pat. 18027, B. 1882, p. 1351; S. C. I. 1882, p. 224; addition, No. 30077, March 1, 1884, B. 1885, p. 89.
Aug. 9	Two similar or dissimilar amines or sulphonic acids.	Resorcinol and homologues.	Actiengesell. f. Anilinfabrikation, Germ. pat. 18861; S. C. I. 1882, p. 404.
Nov. 17	Amidoazobenzenesulphonic acid.	$\beta$ -Naphthol - monosulphonic acid from $\beta$ -naphthylamine.	Badische Anilin- und Soda-Fabrik, Germ. pat. 20760, B. 1883, p. 448; S. C. I. 1883, p. 275.
1882. Jan. 18.	Same as Germ. pat. No. 18027, March 18, 1881.	$\beta$ -Naphthol - $\alpha$ -sulphonic acid prepared by means of sulphuric acid containing anhydride or chloro-sulphuric acid.	Farbenfabriken vorm. F. Bayer & Co., Germ. pat. 20399, B. 1882, p. 3104; addition to No. 18027, March 18, 1881.
Jan. 24	Naphthionic acid.	Naphthionic acid.	Farb. vorm. F. Bayer & Co. Germ. pat. 1235, S. C. I. 1882, p. 226.
Feb. 25	Amines and their sulphonic acids generally.	Anthrol and dioxyanthracene and their sulphonic acids.	C. Liebermann, Germ. pat. 1668; S. C. I. 1882, p. 226, and Germ. pat. 21178 (Actiengesell.), <i>Ibid.</i> 1883, p. 274.
March 21	Amidoazobenzenesulphonic acids.	$\alpha$ - or $\beta$ -Naphthylamine.	Farbenfabriken vorm. F. Bayer & Co., Germ. pat. 20000, B. 1882, p. 3104; S. C. I. 1882, p. 226.
March 25	Aniline or sulphanilic acid.	Diphenylamine [colour subsequently further sulphonated].	Dahl & Co., Germ. pat. 21903, S. C. I. 1883, p. 243.
March 30	Naphthionic acid.	$\beta$ -Naphthol- $\alpha$ -sulphonic acid.	Farb. vorm. F. Bayer & Co., Germ. pat. 20402, B. 1882, p. 3104; S. C. I. 1883, p. 243.
April 12	Naphthionic acid diazotised and combined with two molecules of naphthylamine-sulphonic acid and then again diazotised ( <i>sic</i> ).	$\beta$ -Naphthol or other phenols.	O. Bredt, Eng. pat. 1730, B. 1883, p. 1121.
April 14	Sulphonic acids of amines or amidoazo-compounds ( <i>e.g.</i> naphthionic acid).	$\alpha$ - or $\beta$ -Naphthylamine.	C. Rumpff, Eng. pat. 1773, B. 1883, p. 1121 (see Germ. pat. 20000, March 21); S. C. I. 1883, p. 172.
May 26	Various amines and sulphonic acids, such as naphthionic acid, amidoazobenzene and sulphonic acids.	$\beta$ -Naphtholtrisulphonic acid.	Farb. vorm. Meister, Lucius und Brüning, Germ. pat. 22038, S. C. I. 1883, p. 243.
July 5	$\beta$ -Naphthylamine monosulphonic acids from Schäffer's $\beta$ -naphtholmonosulphonic acid.	Phenols, oxyphenols, naphthols and their ethers, and sulphonic acids.	Farb. vorm. Brönnner, Germ. pat. 22547, B. 1883, p. 1517, S. C. I. 1883, p. 536.
Aug. 21	Solid cumidine.	Phenols, naphthols and sulphonic acids.	Actiengesell. f. Anilinfab., Germ. pat. 22265 (July), Eng. pat. 3997, S. C. I. 1883, pp. 242, 243.



PATENTS RELATING TO AZO- COLOURING MATTERS—*continued*.

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
Sept. 2	Amidoazoxylene . . .	$\beta$ -Naphtholdisulphonic acids (R and G salt).	Farb. vorm. Meister, Lucius und Brünig, Germ. pat. 22010. Addition to No. 16482, Nov. 14, 1879; S. C. I. 1883, p. 243.
Sept. 9	Amines. . . . .	Aromatic oxy-acids and sulphonic acid of $\beta$ -oxynaphthoic acid.	W. Harmsen, Germ. pat. 22707, B. 1883, p. 1518; S. C. I. 1883, p. 536.
Nov. 8	Aniline and homologues and sulphonic acids, amidoacids, amidoazobenzene, &c.	Chrysoidines and their sulphonic and carb-oxylic acids.	Actiengesell. f. Anilinfab., Germ. pat. 22714, B. 1883, p. 1519; S. C. I. 1884, p. 28.
Nov. 30	Amines and sulphonic acids.	Phenols, amines, and sulphonic acids (colour subsequently brominated).	Soc. Anon. d. Mat. Color., Eng. pat. 5696; S. C. I. 1883, p. 411; Germ. pat. 26642, Dec. 14, B. 1884, p. 188.
1883. Jan. 23.	$\beta$ -Naphthylamine mono- and polysulphonic acids from corresponding $\beta$ -naphthol acids.	Amines and phenols	L. Landshoff, Germ. pat. 28378. Addition to No. 22547, July 5, 1882, B. 1884, p. 267.
Feb. 9	Amines and amidoazo- compounds.	$\beta$ -Naphtholmono- and trisulphonic acids.	I. Levinstein, Eng. pat. 706, B. 1884, p. 189.
Feb. 24	Amidonaphthalene disulphonic acids prepared by nitrating and reducing $\alpha$ - and $\beta$ -disulphonic acids of naphthalene.	Phenols and amines	Louis Freund, Germ. pat. 27346, B. 1884, p. 266, and S. C. I. 1884, p. 166. [See also Eng. pat. No. 2104, April 25, 1883, by Dittler & Co., S. C. I. 1884, p. 243.]
	Amines . . . . .	Amidonaphthalene di-sulphonic acids.	
	Amines . . . . .	Naphtholdisulphonic acids from the above amido-acids.	
Feb. 27	Aniline and homologues, amidoazobenzene, the naphthylamines, benzidine.	New $\alpha$ -naphtholmono-sulphonic acids.	Verein chem. Fab., Germ. pat. 26012, B. 1884, p. 60, and S. C. I. 1884, p. 29.
May 5	Amines, &c. . . . .	$\alpha$ -Naphtholmonosulphonic acid (?)	Dahl & Co., Eng. pat. 2296, S. C. I. 1884, p. 29.
July 16	Amines, &c. . . . .	$\alpha$ -Naphtholmonosulphonic acid from $\alpha$ -naphthol acetate.	H. Baum, Eng. pat. 3498 (provis. protec. only), S. C. I. 1884, p. 243.
July 17	Amines, &c. . . . .	$\beta$ -Naphtholdisulphonic acid from Schäffer's monosulphonic acid.	H. Baum, Eng. pat. 3523 (provis. protec. only), S. C. I. 1884, p. 244.
July 31	Amines, &c. . . . .	Fluorol, acenaphthol, and their sulphonic acids.	R. Holliday and W. R. Hodgkinson, Eng. pat. 3730; S. C. I. 1884, p. 319. Also Eng. pat. 3971, Aug. 16, 1883; S. C. I. 1884, p. 244.
Sept. 28	Fluorylamine and acenaphthylamine.	Phenols and sulphonic acids.	
	The amidobenzoic acids and other amidocarboxylic acids.	Diphenylamine or benzylaniline.	Soc. Anon. d. Mat. Color., Eng. pat. 4621; S. C. I. 1884, p. 319; B. 1885, p. 10.
Nov. 24	Aniline and homologues, the naphthylamines, amidoazobenzene, &c.	Sulphonic acids of $\alpha$ -naphthol.	L. Vignon & Co., Eng. pat. 5515 (provis. protec. only), S. C. I. 1884, p. 442; B. 1884, p. 453.
Dec. 5	Di-, tri-, and tetrasulphonic acids of benzidine; mono- and disulphonic acids of benzidinesulphone.	Amines and phenols and their sulphonic acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 25954; B. 1884, p. 366.
Dec. 13	Di- and trisulphonic acid of the amidoazo- compound produced by the action of diazoazobenzene and its homologues upon $\alpha$ - or $\beta$ -naphthylamine monosulphonic acid and subsequent sulphonation.	Phenols, naphthols and their sulphonic acids.	L. Paul, Germ. pat. 28820, B. 1884, p. 545.

PATENTS RELATING TO AZO- COLOURING MATTERS—*continued*.

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
1884. Jan. 5.	Aniline and homologues, nitrilines, naphthylamines, amido-azo- compounds, &c. $\beta$ -Naphthylamine - disulphonic acid.	$\beta$ -Naphthol- $\gamma$ -disulphonic acid. Amines and phenols and sulphonic acids.	Leo Gans and Meinhard Hoffmann, Eng. pat. 816; S. C. I. 1884, p. 567, and amendment, <i>ibid.</i> 1885, p. 742.
Jan. 9	Benzidine-disulphonic acid.	Naphthylamines, methylaniline, methyl-naphthylamine, and sulphonic acids.	J. P. Griess, Eng. pat. 1074; S. C. I. 1885, p. 52; B. 1885, p. 88.
Jan. 9	Benzidine-tri- and tetrasulphonic acids and benzidinesulphone-mono- and disulphonic acids.	Amines, phenols and sulphonic acids.	J. P. Griess, Eng. pat. 1099; S. C. I. 1885, p. 52; B. 1885, p. 88.
Feb. 19	Tolidine-disulphonic acid and bromine derivative.	Phenols.	Verein chem. Fab., Germ. pat. 29957, B. 1885, p. 10; S. C. I. 1885, p. 452.
Feb. 27	Benzidine and homologues.	Naphthylamines and sulphonic acids.	P. Böttiger, Germ. pat. 28753, B. 1884, p. 453; S. C. I. 1885, p. 278; also Germ. pat. 39096, Aug. 29, 1885, and 43125, July 29, 1887, B. 1888, p. 324.
Feb. 27	Amines and sulphonic acids.	$\alpha$ -Naphtholdisulphonic acid.	L. Vignon & Co., Germ. pat. 32291, B. 1885, p. 675; S. C. I. 1885, p. 452.
March 2.	New $\beta$ -naphthylamine-mono-sulphonic acid. Naphthionic acid.	$\alpha$ - and $\beta$ -naphtholsulphonic acids. $\beta$ -Naphtholmonosulphonic acid from new $\beta$ -naphthylamine-sulphonic acid.	Dahl & Co., Germ. pat. 29084, B. 1885, p. 9. [See also Germ. pat. 30640, May 20, 1884, B. 1885, p. 167 and 32276, Nov. 24, 1884; also Eng. pat. 7713, May 14, 1884; S. C. I. 1885, p. 53.]
May 1	Amines and sulphonic acids.	$\beta$ -Naphtholdisulphonic acids separated by fractional salting out of acid sodium salts.	Leipziger Anilinfabrik, Eng. pat. 7097, S. C. I. 1885, p. 339; B. 1886, p. 75.
May 1	Amines and sulphonic acids.	$\beta$ -Naphtholmonosulphonic acids separated as above.	Leipziger Anilinfabrik, Eng. pat. 7098, S. C. I. 1885, p. 339.
June 9	Diamido - oxysulphobenzide and homologues.	Phenols and sulphonic acids.	Farb. vorm. Meister, Lucius und Brünig, Eng. pat. 8744, S. C. I. 1885, p. 400.
June 10	Sulphanilic and naphthionic acids.	Phenols; in presence of acetic acid instead of alkali.	R. Krügener and the Farb. vorm. Brönnner, Eng. pat. 8806, S. C. I. 1885, p. 400.
June 14	Benzidine and homologues.	Salicylic acid and isomerides.	Farb. vorm. F. Bayer & Co., Germ. pat. 31658, B. 1885, p. 394; S. C. I. 1885, p. 400.
June 28	Sulphonic acid of benzene-azaoamidoxylenes.	$\beta$ -Naphthol- $\alpha$ -sulphonic acid.	Farb. vorm. F. Bayer & Co., Eng. pat. 9518; S. C. I. 1885, p. 453.
July 1	Tolidine and diamidodixyl.	Salicylic acid.	Farb. vorm. F. Bayer & Co., Eng. pat. 9606, S. C. I. 1885, p. 491.
Oct. 7	Paraphenylene-diamine.	Metaphenylene-diamine.	P. Monnet & Co., Germ. pat. 32502, B. 1885, p. 676.
Nov. 20	Sulphonic acids of aniline and homologues.	Benzidine and homologues.	Farb. vorm. F. Bayer & Co., Germ. pat. 32958, B. 1885, p. 686.
1885. Jan. 20.	Mono- and disulphonic acids of benzidinesulphone.	Amines, phenols and sulphonic acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 33088, B. 1885, p. 723.
March 14	Tolidine and diamido-dixyl.	Naphthylamines and sulphonic acids.	Farb. vorm. F. Bayer & Co., Eng. pat. 3803, S. C. I. 1886, p. 96.
March 17	Tolidine.	Mono- and disulphonic acids of the naphthylamines.	Actiengesell. f. Anilinfab., Germ. pat. 35615; addition to No. 28753, February 27, 1884, B. 1886, p. 473.

PATENTS RELATING TO AZO- COLOURING MATTERS—*continued*.

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
June 25 .	Thio-paratoluidine (Merz and Weith's)	Naphthol and naphthyl- aminesulphonic acids.	Dahl & Co., Germ. pat. 34299, B. 1886, p. 71, S. C. I. 1886, p. 96.
July 31 .	Amidoazo- $\alpha$ - naphthalenedi- sulphonic acid (from $\alpha$ - naphthylamine diazodi- sulphonic acid and $\alpha$ - naph- thylamine).	Amines, phenols, and sulphonic acids.	M. Hoffmann and A. Weinberg, Eng. pat. 9214, S. C. I. 1886, p. 427. [See also Germ. pat. 39029, July 3, 1885, of L. Casella & Co., B. 1887, p. 273.]
August 1 .	Tolidine. . . . .	The naphthols and their sulphonic acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 35341, B. 1886, p. 422, S. C. I. 1886, p. 427.
August 5 .	Metanitriline and homo- logues, metanitroamido- benzoic acid, &c.	Metaphenylenediamine and homologues	A. Leonhardt & Co., Germ. pat. 37021, B. 1886, p. 803; S. C. I. 1886, p. 523.
Aug. 27 .	Paranitriline . . . .	$\beta$ - Naphthylamine mono- sulphonic acid corre- sponding to Schäffer's $\beta$ - naphtholsulphonic acid.	Farb. vorm. Brönnner, Germ. pat. 36757; addition to No. 22547, July 5, 1882; B. 1886, p. 638; S. C. I. 1886, p. 523.
Oct. 18 .	Amines and sulphonic acids.	Sulphurised naphthols.	Dahl & Co., Germ. pat. 35788, B. 1886, p. 639.
Nov. 7 .	Thio - paratoluidine (m.p. 175°).	Phenols, amines, and sulphonic acids.	Dahl & Co., Germ. pat. 35790, B. 1886, p. 639.
Nov. 24 .	Diamidodianisoil and homo- logues.	Phenols, amines, and sulphonic acids.	Farb. vorm. F. Bayer & Co., Eng. pat. 14424, S. C. I. 1886, p. 428; Germ. pat. 38802, Nov. 19, 1885, B. 1887, p. 272.
Dec. 12 .	Benzidine and homologues .	Two dissimilar amines, phenols, or sulphonic acids.	Actiengesell. f. Anilinfab., Eng. pat. 15296, S. C. I. 1886, p. 595; Germ. pat. 39096, August 29, 1885, B. 1877, p. 273.
Dec. 21 .	Amines and sulphonic acids.	Naphtholdisulphonic acids from naphthal- enetrisulphonic acids.	C. Rudolph and O. Güreke, Eng. pat. 15716, S. C. I. 1886, p. 662; Germ. pat. 38281, Sep- tember 2, 1885, B. 1887, p. 125.
Dec. 22 .	Amines and sulphonic acids.	Naphtholdisulphonic acid from nitronaph- thalenesulphonic acid.	Schöllkopf Aniline and Ch. Co., Eng. pat. 15775, S. C. I. 1886, p. 164; Germ. pat. 40571, Dec. 23, 1885, and addition 42304, Jan. 28, 1886, B. 1887, p. 203.
Dec. 22 .	Amines and sulphonic acids.	Naphtholmonosulphonic acid from nitronaph- thalenesulphonic acid.	Schöllkopf Aniline and Ch. Co., Eng. pat. 15781, S. C. I. 1886, p. 164.
1886. Jan. 28.	Benzidine and homologues .	One mol. of a phenol or amidosulphonic acid and then a second mol. of a dissimilar amine, phenol, sulphonic, or carboxylic acid.	Actiengesell. f. Anilinfab., Germ. pat. 40954, B. 1888, p. 71.
Jan. 29 .	Diamidostilbenedisulphonic acid from paranitrotoluene- sulphonic acid.	Amines, phenols, sul- phonic, and carboxylic acids.	A. Leonhardt & Co., Germ. pat. 38735, B. 1887, p. 183, Eng. pat. 4387, March 29.
Feb. 9 .	Diamidodiphenol-ethers .	Two dissimilar amines, phenols, sulphonic or carboxylic acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 40247, B. 1887, p. 614. Addition to Pat. 38802, Nov. 19, 1885 (Eng. pat. Nov. 24, 1885).
Feb. 15 .	Benzidine and homologues.	Two dissimilar phenols, amines, sulphonic or carboxylic acids.	C. A. Martius, Eng. pat. 2213, S. C. I. 1887, p. 138. [See also Eng. pat. 15296, Dec. 12, 1885.]
Feb. 17 .	Benzidinemonosulphonic acid.	Two similar or dis- similar amines, phe- nols, sulphonic or car- boxylic acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 38664, B. 1887, p. 271, Eng. pat. 3198, March 6, 1887, S. C. I. 1887, p. 285.



PATENTS RELATING TO AZO-COLOURING MATTERS—*continued*.

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
March 16	Benzidinemonosulphonic acid.	Phenols, amines, &c.	T. Carnelley, Eng. pat. 3890, S. C. I. 1887, p. 138.
March 31	Amidoazobenzenedisulphonic acid.	Paratolyl- $\beta$ -naphthyl-amine.	Actiengesell. f. Anilinfab., Germ. pat. 38425, B. 1887, p. 155, Eng. pat. (Schad) 9754, July 28, 1886; S. C. I. 1887, p. 523.
April 14	Azo-compounds produced by the action of diazotised amidosulphonic acids of benzene and homologues and benzidine and homologues on $\alpha$ -naphthylamine.	Naphthols and their sulphonic acids.	L. Casella & Co., Germ. pat. 40977, B. 1888, p. 71. Addition to pat. 39029, July 3, 1885.
April 29	$\beta$ -Naphthylamine- $\delta$ -mono-sulphonic acid. Amines and sulphonic acids.	Phenols, amines, and their sulphonic acids. $\beta$ -Naphthylamine- $\delta$ -monosulphonic acid.	Farb. vorm. F. Bayer & Co., Eng. pat. 5846, S. C. I. 1887, p. 436; Germ. pat. 39925, April 15, 1886, B. 1887, p. 613 and 42021, April 15, 1886, B. 1888, p. 120. Additional Germ. pat. 41505, Dec. 17, 1886, B. 1888, p. 75; 42272, Jan. 1, 1887, B. 1888, p. 112; 42273, Jan. 23, 1887, B. 1888, p. 113.
May 22	Paradiamines of stilbene and fluorene.	Two similar or dissimilar amines, phenols, sulphonic, or carboxylic acids.	Actiengesell. f. Anilinfab., Germ. pat. 39756, Eng. pat. (Martius) 7284, May 31; S. C. I. 1887, p. 437. Additional Germ. pat. 43142, March 22; and 43197, April 20, B. 1888, p. 324.
May 28	Benzidine and homologues.	Meta-diamines and their sulphonic acids.	Oehler, Germ. pat. 40905, B. 1887, p. 754, Eng. pat. 4492, March 25, 1887, S. C. I. 1888, p. 120.
May 31	Diamido-derivatives of di-phenol-ethers.	Two similar or dissimilar amines, phenols, sulphonic, or carboxylic acids.	C. A. Martius, Eng. pat. 7283, S. C. I. 1887, p. 139.
June 6	Diamidodiphenylketone, its hydrol and their sulphonic acids.	Phenols, amines, and sulphonic acids.	H. Wichelhaus, Germ. pat. 39958, B. 1887, p. 613.
June 18	Thiobenzidine and thio-tolidine.	Monosulphonic acids of $\alpha$ - and $\beta$ -naphthylamine.	Dahl & Co., Germ. pat. 38795, B. 1887, p. 272.
Aug. 25	Azo-compounds produced by combining <i>m</i> - and <i>p</i> -sulphanilic acid and homologues with $\alpha$ -naphthylamine.	Metaphenylene diamine and homologues, resorcinol.	A. Poirrier, &c., Germ. pat. 42992, B. 1888, p. 270.
Oct. 5	New $\alpha$ -naphthylaminedisulphonic acid.	Naphthols and their sulphonic acids; the naphthylamines.	Dahl & Co., Germ. pat. 42440, B. 1888, p. 204; also Germ. pat. 41957, Sept. 4, 1886; B. 1888, p. 119.
Oct. 5	Metadiamidodiphenyldicar-bonic acid and ethers.	Amines, phenols and sulphonic acids.	L. Paul, Germ. pat. 41819, B. 1888, p. 120. Additional Germ. pat. 44089, Feb. 26, 1887; B. 1888, p. 766, and 44161, June 24, 1887; B. 1888, p. 767.
Oct. 8	Amines and their sulphonic acids.	Dioxynaphthalenesulphonic acid from naphthalenetrisulphonic acid.	Actiengesell. f. Anilinfab., Germ. pat. 42270, B. 1888, p. 156; also Germ. pat. 42261, B. 1888, p. 157.
Oct. 9	Amines, amidoazo-compounds, benzidine, anisidine, &c., and their sulphonic acids.	$\beta$ -Naphthol-F-sulphonic acid from Ebert & Merz's $\alpha$ -naphthalenedisulphonic acid.	L. Casella & Co., Eng. pat. 12908, S. C. I. 1887, p. 725; Germ. pat. 42112, Sept. 22, 1886; B. 1888, p. 117; additional pat. 45221, June 4, 1887; B. 1888, p. 877.

PATENTS RELATING TO AZO- COLOURING MATTERS—*continued.*

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
	$\beta$ -Naphthylamine-F-sulphonic acid from the naphthol-F-sulphonic acid.	Amines, phenols, and sulphonic acids.	
Oct. 19	Amines and their sulphonic acids. Benzidineorthodisulphonic acid.	$\beta$ -Naphthylamine-F-sulphonic acid. Two similar or dissimilar amines, phenols, or sulphonic acids.	Actiengesell. f. Anilinfab., Germ. pat. 43100, B. 1888, p. 323.
Oct. 27	Orthosulphonic and ortho-carboxylic acids of benzidine.	Phenols, amines, and sulphonic acids.	Actiengesell. f. Anilinfab. Eng. pat. 13780, S. C. I. 1887, p. 138.
Nov. 9	$\alpha$ -Naphthylenc-diamine	Naphthol and naphthylamine sulphonic acids, salicylic acid, &c.	Badische Anilin- u. Soda-Fab., Germ. pat. 39954, B. 1887, p. 614, S. C. I. 1887, p. 726.
Nov. 11	Diazoamido- compounds	Heated with phenols	Fischer & Michaelis, Germ. pat. 40890, B. 1887, p. 754.
Dec. 2	Symmetrical paradiamido-azobenzene.	Naphthol and naphthylamine sulphonic acids.	Actiengesell. f. Anilinfab., Germ. pat. 40740, B. 1887, p. 668.
Dec. 7	Amido-compounds generally	Naphtholtrisulphonic and dioxynaphthalenedisulphonic acids from naphthalenetetra-sulphonic acid.	Farb. vorm. F. Bayer & Co., Germ. pat. 40893, B. 1887, p. 754.
Dec. 14	Diamidostilbenedisulphonic acid.	Two similar or dissimilar amines, phenols, sulphonic or carboxylic acids.	A. Leonhardt & Co., Germ. pat. 40575, Ber. 1887, p. 668; Eng. pat. (amended) 4387, March 29, 1886; S. C. I. 1888, p. 319. Additional Germ. pat. 42466, Nov. 16, 1886; B. 1888, p. 269; Eng. pat. 3994, March 16, 1887; S. C. I. 1888, p. 319.
Dec. 30	Benzidine and homologues, diamidoanisole, diamidostilbene and fluorene, &c.	Alkyl-derivatives of the naphthylamines and their sulphonic acids.	Farb. vorm. F. Bayer & Co., Eng. pat. 17083, S. C. I. 1888, p. 31; Germ. pats. 41761, Dec. 21, 1886; B. 1888, p. 72; 43169, March 24, 1887; B. 1888, p. 382; 43204, June 8, 1887; B. 1888, p. 383.
1887. Feb. 1	Amidoazobenzene, p-nitraniline, amidonaphthalene, azobenzenesulphonic acids.	Alkyl-derivatives of $\beta$ -naphthylaminesulphonic acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 41510, B. 1888, p. 71. Additional pat. 42771, Dec. 28, 1887, B. 1888, p. 269.
Feb. 22	Paradiamidodiphenylamine	Two similar or dissimilar naphthol or naphthylaminesulphonic acids.	Dahl & Co., Germ. pat. 40745, B. 1887, p. 668.
Feb. 22	Paraphenylene-diamine	Naphtholsulphonic acids	Badische Anilin- u. Soda-Fab., Germ. pat. 42011, B. 1888, p. 268. Additional pat. 42814, April 19, 1887, B. 1888, p. 268.
Feb. 26	Amidoazo- compounds from tetrazodiphenyl and ditolyl and two mols. of aniline or homologues.	Naphthols, naphthylamines, and their sulpho-acids.	Leipziger Anilinfab., Germ. pat. 44881; B. 1888, p. 876.
March 5	Benzidine and homologues	Amidoazobenzenesulphonic acids, and homologues. Product afterwards decomposed by salts of naphthylaminesulphonic acids.	Actiengesell. f. Anilinfab., Germ. pat. 41362, B. 1888, p. 70. Addition to No. 28753 (Böttiger), Feb. 27, 1884.
March 8	Diamidodibenzeneazodiphenyl and homologues.	Resorcinol, oreinol, and naphthionic acid.	E. Kegel, Germ. pat. 42227, B. 1888, p. 156.
March 15	Amines and their sulphonic acids.	$\beta$ -Naphtholdisulphonic acid from $\beta$ -naphthol-F-monosulphonic acid.	L. Casella & Co., Germ. pat. 44079; B. 1888, p. 767.
March 21	Benzidine and homologues	Mono- and disulphonic acids of dioxynaphthalene.	W. Majert, Eng. pat. 4243, S. C. I. 1888, p. 320.

PATENTS RELATING TO AZO- COLOURING MATTERS—*continued.*

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
March 22	Diamidostilbene . . .	$\alpha$ -Naphtholdisulphonic acid of Germ. pat. 40571, Dec. 23, 1885 (Schöllkopf).	Actiengesell. f. Anilinfab., Germ. pat. 43142, B. 1888, p. 324. 1st addition to 39756, May 22, 1886.
March 30	Benzidine and homologues .	One mol. $\beta$ -naphthyl-aminedisulphonic acid R and one mol. of another amine, phenol, or sulphonic acid.	Actiengesell. f. Anilinfab., Germ. pat. 41095, B. 1888, p. 70. Addition to No. 28753 (Böttiger), Feb. 27, 1884.
April 20.	Diamidostilbene . . .	One mol. $\alpha$ -naphtholdisulphonic acid of pat. 4057 (1885) Schöll. and a second mol. of a dissimilar phenol or sulphonic acid.	Actiengesell. f. Anilinfab., Germ. pat. 43197, B. 1888, p. 324. 2nd addition to 39756, May 22, 1886.
April 22.	Amidosulphonic acids of mixed tertiary aromatic amines.	Phenols, amines, and sulphonic acids.	A. Kern, Eng. pat. 5896, S. C. I. 1888, p. 498.
April 23.	Benzidine and tolidine .	One mol. $\alpha$ -naphtholdisulphonic acid and one mol. of an amine, phenol, or sulphonic acid.	Actiengesell. f. Anilinfab., Germ. pat. 43493, B. 1888, p. 491. 1st addition to pat. 40954, Jan. 28, 1886.
April 23.	Benzidine and tolidine .	One mol. salicylic acid, and then a second mol. of a phenol, amine, or sulpho-acid.	Farb. vorm. F. Bayer & Co., Germ. pat. 44797, 1st addition to No. 31658, June 14, 1884; B. 1888, p. 813.
April 23.	Aromatic amines . . .	Ethers of <i>m</i> -amido-phenyllutidinedicarboxylic acid.	Farb. vorm. Meister, Lucius and Brä., Germ. pat. 42295; B. 1888, p. 204.
May 6 .	Ethers of <i>m</i> -amido-phenyllutidinedicarboxylic acid.	Phenols, amines and sulpho-acids.	Actiengesell. f. Anilinfab., Eng. pat. 6687, S. C. I. 1888, p. 430.
	Diazoamidosulphonic acids from benzidine and homologues.	Naphthionic acid, &c.	
	Benzidine and homologues .	One mol. of naphthyl-aminedisulphonic acid, or of salicylic acid and another mol. of an amine, phenol, or sulphonic acid.	
	Paradiamidoazobenzene .	Amines, phenols, and sulphonic acids.	
May 21 .	Unsymmetrical substituted diphenyl bases.	Two similar or dissimilar phenols, amines, sulphonic or carboxylic acids.	R. Geigy, Germ. pat. 42006, R. 1888, p. 74.
May 28 .	Amines, &c. . . . .	New monosulphonic acid of $\alpha$ -naphthol.	Liebmann & Studer, Eng. pat. 7812; S. C. I. 1888, p. 43.
June 1 .	Naphthionic acid . . .	Naphthionic acid.	Wichelhaus & Krohn, Germ. pat. 42382, B. 1888, p. 203.
June 8 .	Amines generally . . .	$\beta$ -Naphthol- $\delta$ -disulphonic acid.	L. Casella & Co., Eng. pat. 8265, S. C. I. 1888, p. 431.
June 9 .	Metadiphenyl acid of benzidine.	Two similar or dissimilar amines, phenols, or sulphonic acids.	L. Paul, Eng. pat. 8296; S. C. I. 1888, p. 432.
June 11 .	Amidoazobenzidines from diazotised benzidine, homologues and derivatives and two similar or dissimilar amines.	Two similar or dissimilar amines, phenols, or sulphonic acids.	L. Paul, Eng. pat. 8437; S. C. I. 1888, p. 432.
June 15 .	Ethers of diamido-diphenol.	Two mols. $\alpha$ -naphthol-monosulphonic acid (Armstrong's), or one mol. of this acid and then a second mol. of a different phenol, amine, or sulpho-acid.	Farb. vorm. F. Bayer & Co., Germ. pat. 44650, 2nd addition to No. 38802, Nov. 19, 1885; B. 1888, p. 818.



PATENTS RELATING TO AZO- COLOURING MATTERS—*continued.*

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
June 24 .	Diamidodibenzeneazoditolyl.	Resorcinol and naphthionic acid.	Leipziger Anilinfab., Germ. pat. 43486; B. 1888, p. 681. Addition to No. 42227 (Kegel), March 8, 1887.
June 29 .	Amidoazo- compounds from diazotised amidosulphonic acids of benzene and homologues and $\alpha$ -naphthylamine.	Metadiamines or resorcinol.	Soc. Anon. d. Mat. Col., Eng. pat. 9257, S. C. I. 1888, p. 432.
June 30 .	Amines and sulphonic acids.	New $\alpha$ -naphthylamine-monosulphonic acid.	Ewer & Pick, Germ. pat. 42874, B. 1888, p. 325.
June 30 .	Metanitraneline or <i>m</i> -toluidine reduced in alkaline solution.	Phenols, amines, sulphonic, or carboxylic acids.	Soc. Anon. d. Mat. Col., Eng. pat. 9315, S. C. I. 1888, p. 499; also Germ. pat. 44045, July 27, 1887, B. 1888, p. 766.
July 2 .	Diamidobenzil from di-nitrobenzoin.	Amines, phenols, sulphonic, or carboxylic acids.	Soc. Anon. d. Mat. Col., Eng. pat. 9414; S. C. I. 1888, p. 432. Germ. pat. 41269, Aug. 28, 1887, B. 1888, p. 816.
July 4 .	Paranitraneline . . .	$\alpha$ -Naphthylaminedisulphonic acid.	R. Geigy, Eng. pat. 9468; S. C. I. 1888, p. 433.
July 29 .	Benzidine and tolidine .	One mol. $\alpha$ -amidonaphthalene- $\delta$ -disulphonic acid (Schöll.) and a second mol. of an amine, phenol, &c.	Actiengesell. f. Anilinfab., Germ. pat. 43125, B. 1888, p. 324. Addition to 28753, Feb. 27, 1884.
Aug. 18 .	Amines and sulphonic acids.	$\alpha$ -Naphtholdisulphonic acid.	A. Leonhardt & Co., Eng. pat. 11318, S. C. I. 1888, p. 672.
Sept. 1 .	Benzidine, tolidine, diamidodiansoil, diamidodiphenetol, diamidostilbene and sulphonic acids.	Naphthylamines and sulphonic acids. Products alkylated.	Actiengesell. f. Anilinfab., Eng. pat. 11880, S. C. I. 1888, p. 563.
Sept. 3 .	Nitrotoluidine m.p. 78° and nitroxylidine m.p. 123° reduced in alkaline solution.	Phenols, amines, sulphonic and carboxylic acids.	Soc. Anon. d. Mat. Col., Eng. pat. 11976; S. C. I. 1888, p. 563; Germ. pat. 44554, Sept. 6, 1887, B. 1888, p. 817.
Sept. 12 .	Diamido- derivatives of phenyloxytolyl-ethers and their homologues.	Two mols. of an amine, phenol, sulphonic, or carboxylic acid.	Soc. Anon. d. Mat. Col., Eng. pat. 12355, S. C. I. 1888, p. 563.
Sept. 19 .	Nitranelines and homologues.	$\alpha$ -Naphthylaminemonosulphonic acid (Witt's).	Soc. Anon. d. Mat. Col., Eng. pat. 12692, S. C. I. 1888, p. 564.
Sept. 19 .	Aniline and homologues, the naphthylamines and their sulphonic acids.	Extract of fustic or mahogany.	C. S. Bedford, Eng. pat. 12667, S. C. I. 1888, p. 619.
Sept. 22 .	$\beta$ -naphthylamine-F-sulphonic acid.	Amines and phenols .	L. Casella & Co., Germ. pat. 43740, B. 1888, p. 557.
Sept. 25 .	Nitranelines and homologues, nitronaphthylamines, &c.	$\alpha$ -naphthylaminemonosulpho- acid (Witt's).	Soc. Anon. d. Mat. Col., Germ. pat. 45787, addition to 6715 Nov. 19, 1878; B. 1889, p. 40.
Sept. 27 .	Sulpho-acids of alkyloxy-diamido-diphenyl bases.	Amines, phenols, sulpho- and carboxylic acids.	L. Casella & Co., Germ. pat. 44209; B. 1888, p. 814.
Oct. 12 .	Diamido-diphenol ethers and homologues.	Two similar or dissimilar phenols, amines, or sulpho- acids.	L. Casella & Co., Germ. pat. 46134; B. 1889, p. 82.
Oct. 23 .	Aromatic amido- compounds.	New dioxynaphthalene .	Ewer and Pick, Germ. pat. 45229; B. 1888, p. 916.
Oct. 24 .	Alkyl-ethers of oxybenzidine and analogous bases.	Two similar or dissimilar amines, phenols, sulphonic or carboxylic acids.	A. Weinberg, Eng. pat. 14464, S. C. I. 1888.
Oct. 28 .	Orthodiamidodiphenic acid .	Amines, phenols, and their sulphonic acids	Badische Anilin- u. Soda-Fab., Germ. pat. 43524; B. 1888, p. 492.
Nov. 1 .	Diamidotriphenylmethane .	$\beta$ -Naphtholdisulphonic acid (R salt).	Leipziger Anilinfab., Germ. pat. 43644, B. 1888, p. 555.

PATENTS RELATING TO AZO-COLOURING MATTERS—*continued.*

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
Nov. 1	Sulpho- acids of alkyl-oxy-diamidodiphenyl bases.	Amines, phenols, sulpho- and carboxylic acids.	L. Casella & Co., Germ. pat. 44770, addition to 44209 above; B. 1888, p. 814.
Nov. 4	$\alpha\alpha$ - Naphthylene - diamine (m.p. 188°-190°).	Amines, phenols, sulpho- and carboxylic acids.	Ewer and Pick, Germ. pat. 45549; B. 1888, p. 922.
Nov. 7	Benzidine and tolidine.	Two mols. of the sulphonic acid of ethyl-aniline or diphenylamine; or one mol. of these and a second mol. of different amine, phenol, or sulphonic acid.	G. C. Zimmer, Eng. pat. 15154, S. C. I. 1888.
Nov. 10	Paradiamines generally	Chrysoidines and their sulpho- acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 44954; B. 1888, p. 876.
Nov. 10	Amidosulpho- acids of benzene and homologues, sulpho- acids of amidoazobenzene and homologues, of benzidine and homologues, diamidostilbene, &c.	Bismarck brown.	Farb. vorm. F. Bayer & Co., Germ. pat. 46804; B. 1889, p. 176.
Nov. 11	Bismarck brown and toluylene brown.	Metaphenylene and <i>m</i> -toluylene diamines.	H. Kupferberg, Germ. pat. 46375; B. 1889, p. 176.
Nov. 11	Benzidine and tolidine.	Phenol and orthoeresol.	P. Forel, Eng. pat. 15459, S. C. I. 1888, p. 320.
Nov. 18	Dinitraniline (Gottlieb's)	Mono- and disulphonic acids of $\beta$ -naphthylamine.	O. N. Witt, Germ. pat. 44171; B. 1888, p. 813.
Nov. 18	New naphthylene-diamines.	Amines, phenols and their sulpho- acids.	Ewer and Pick, Germ. pat. 45788, addition to 45549 above; B. 1889, p. 42.
Nov. 30	Amidoazo- compounds from tetrazo-salts of <i>p</i> -diamines and their sulphonic or carboxylic acids with $\alpha$ -naphthylamine.	Amines, phenols, sulphonic or carboxylic acids	Farb. vorm. F. Bayer & Co., Eng. pat. 16484, S. C. I. 1888, p. 619.
Nov. 30	Paradiamines and sulphonic acids, naphthionic acid, &c.	Chrysoidine and Bismarck brown.	Farb. vorm. F. Bayer & Co., Eng. pat. 16493, S. C. I. 1888, p. 619.
Dec. 9	Diamidobenzil	Two dissimilar amines, phenols, or sulpho-acids.	Poirrier and Rosenstiehl, Germ. pat. 45789, addition to 44269, Aug. 28, 1887; B. 1889, p. 41.
Dec. 19	Naphthionic acid &c. (2 mols.)	One mol. benzidine, tolidine, diamidostilbene &c.	Worms, Eng. pat. 17466; S. C. I. 1888, p. 839.
Dec. 21	Metanitriline and homologues, nitronaphthylamines, orthonitriline-sulphoacid, &c.	Salicylic and $\alpha$ -oxy-naphthoic acid.	Nietzki, Eng. pat. 17583; S. C. I. 1888, p. 839, Germ. pat. 44170, Nov. 16, 1887; B. 1888, p. 812.
Dec. 21	Diamido-diphenol ethers	Two mols. $\alpha$ -naphthol-monosulpho- acid (Sch.) or one mol. of this acid and a second mol. of a different phenol, amine, or sulpho- acid.	Farb. vorm. F. Bayer & Co., Germ. pat. 44775; B. 1888, p. 872, 3rd addition to 38802, Nov. 19, 1885.
Dec. 24	Primary aromatic amines	Bismarck brown; product afterwards sulphonated.	Farb. vorm. F. Bayer & Co., Germ. pat. 47066, B. 1889, p. 313. 1st addition to 46804, Nov. 10, 1887.
Dec. 30	Dinitraniline (Gottlieb's)	Sulpho- acids of the naphthylamines.	Actiengesell. f. Anilinfab., Eng. pat. 17952; S. C. I. 1888, p. 839.
1888. Jan. 10.	Mono- and disulpho- acids of benzidine and tolidine.	Amines, phenols, and their sulpho- acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 44779, B. 1888, p. 873.

PATENTS RELATING TO AZO- COLOURING MATTERS—*continued.*

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
Jan. 24	Benzidine and tolidine.	Meta-oxytoluic acid	Farb. vorm. F. Bayer & Co., Germ. pat. 44906, 2nd add. to 31658, June 14, 1884, B. 1888, p. 814.
Jan. 28	One mol. benzidine, tolidine, diamidodiphenol ethers, &c.	Two mols. $\beta$ -naphthol- $\delta$ -monosulpho- acid or of $\alpha$ -naphthol- di- sulpho- acid (Sch.). Or 1 mol. $\delta$ - or Sch.- acid and a second mol. of $\alpha$ - or $\beta$ - naphthol or their sulpho- acids.	Farb. vorm. F. Bayer & Co., Eng. pat. 1346, S. C. I. 1889, p. 41.
Feb. 2	Phenylenediamine (? para)	Phenols, amidosulpho- or carboxy- acids.	R. Williams, Eng. pat. 1593, S. C. I. 1889, p. 279.
Feb. 9	Tolidinesulphone and its mono- and disulpho- acid.	Ammones, phenols, and their sulpho- acids.	Farb. vorm. F. Bayer & Co., Germ. pat. 44784; add. to 33088, Jan. 20, 1885, B. 1888, p. 874.
Feb. 10	Amidoazonaphthalenes and their mono- and disulpho- acids.	Bismarek brown	Farb. vorm. F. Bayer & Co., Germ. pat. 47067, B. 1889, p. 313. 2nd addition to 46804, Nov. 10, 1887.
Feb. 25	Para- and metanitriline, <i>m</i> - nitro- <i>p</i> - toluidine (m.p. 77°).	Cresotinic and $\alpha$ -oxy- naphthoic acid.	Nietzki, Germ. pat. 46203; add. to 44170, Nov. 16, 1887, B. 1889, p. 117.
March 1	Benzidine and tolidine	One mol. $\alpha$ -naphtholdi- sulpho-acid (Sch.) and a second mol. of another amine, phenol, or sulpho- acid.	Actiengesell. f. Anilinfab., Germ. pat. 45342; 2nd add. to 40954, Jan. 28, 1886, B. 1888, p. 919.
March 16	Aromatic amido- compounds	New $\alpha$ -naphtholdisulpho- acid.	Actiengesell. f. Anilinfab., Germ. pat. 45776, B. 1888, p. 917.
March 18	Diamidotolane . . .	Two similar or dissimilar amines, phenols, or sulpho- acids.	Kalle & Co., Germ. pat. 45371, B. 1888, p. 922.
March 26	Benzidine and homologues, diamidostilbene, &c.	$\alpha$ -naphtholdisulpho-acid of Germ. pat. 45776, above.	Actiengesell. f. Anilinfab., Eng. pat. 4625, S. C. I. 1889, p. 280.
March 29	Diamidostilbene . . .	Two mols. of the $\alpha$ -naphtholdisulphonic acid of pat. 45776 of March 16, or one mol. of this and a second mol. of a dissimilar sulphonic acid.	Actiengesell. f. Anilinfab., Germ. pat. 46971, B. 1889, p. 310. 4th addition to 39756, May 22, 1886.
March 29	Benzidine and tolidine.	Two mols. of the $\alpha$ -naphtholdisulphonic acid of pat. 45776 of March 16, or one mol. of this and a second mol. of dissimilar amine, phenol, or sulphonic acid.	Actiengesell. f. Anilinfab., Germ. pat. 47068, B. 1889, p. 312. 3rd addition to 40954, Jan. 28, 1886.
April 8	Tolidine . . .	$\alpha$ -Amidonaphthalene- $\epsilon$ -disulphonic acid.	Actiengesell. f. Anilinfab., Germ. pat. 46953, B. 1889, p. 311. 6th addition to 28753, Feb. 27, 1884.
April 11	Benzidine and homologues and their sulpho- acids.	Dioxytoluene and homologues, substitution products and sulpho- acids.	R. Williams, Eng. pat. 5404, S. C. I. 1889, p. 280.
April 20	Benzidine, tolidine, diamidostilbene, diamidophenol ethers and sulpho- acids.	$\alpha$ -naphtholdisulpho-acid of Eng. pat. 4625, above.	Actiengesell. f. Anilinfab., Eng. pat. 5909, S. C. I. 1889, p. 280.
April 20	Aromatic monamines, amidoazo- compounds and their sulpho- acids.	New $\alpha$ -naphtholdisulpho- acid, above.	Actiengesell. f. Anilinfab., Eng. pat. 5910, S. C. I. 1889, p. 281.



PATENTS RELATING TO AZO- COLOURING MATTERS—*continued.*

Date	Compound diazotised	Phenol, Amine, or Sulphonic acid	Patentee and reference
April 28.	Sulpho- acids of mono- and dithio- <i>p</i> - toluidine.	Phenols and their sulpho- acids.	Farb. vorm. F. Bayer & Co., Eng. pat. 6319, S. C. I. 1888, p. 620.
May 5.	One mol. of benzidine and homologues.	One mol. of dioxytoluene and a second mol. of a dissimilar dioxy-compound.	R. Williams, Eng. pat. 6743, S. C. I. 1889, p. 281.
June 1.	Compounds formed by combining diazotised amidophenols and their sulpho- acids with $\alpha$ -naphthylamine.	$\beta$ -naphtholmonosulpho- acid (Schäffer's), $\beta$ -naphtholdi- sulpho- acid (R. salt), $\alpha$ -naphtholmonosulpho- acid (Nev. & Win.).	Oehler, Germ. pat. 45994, B. 1889, p. 82.
June 23.	Sulphanilic acid, &c.	Tetrazo-compound from benzidine, salicylic acid and resorcinol.	Actiengesell. f. Anilinfab., Germ. pat. 46328, B. 1889, p. 117; also add. 46501, B. 1889, p. 178.
July 3.	Azo- colours derived from Resorcinol converted into nitroso- derivatives.	. . . . .	St. v. Kostanecki, Germ. pat. 46479, B. 1889, p. 215.
Aug. 23.	Diamidocarbazol.	Two similar or dissimilar amines, phenols, sulphonic or carboxylic acids.	Badische An. & Soda-Fab., Germ. pat. 46438, B. 1889, p. 177.
Aug. 31.	Amidoazo- compounds condensed by means of phosphene.	. . . . .	Badische An. & Soda-Fab., Germ. pat. 46737, B. 1889, p. 179.
Sept. 14.	Diamidostilbene . . . .	One mol. $\beta$ -naphthylaminedisulphonic acid R., and one mol. of $\alpha$ - or $\beta$ - naphthylamine, or their mono-sulphonic acids.	Actiengesell. f. Anilinfab., Germ. pat. 47026, B. 1889, p. 310. 3rd addition to 39756, May 22, 1886.
Oct. 30.	Benzidine and homologues (1 mol.)	Two mols. of an amido-sulphonic acid afterwards substituted by two mols. of an amine or phenol.	R. Williams, Eng. pat. 15654, S. C. I. 1889, p. 281.

R. M.

**AZODIPHENYL BLUE** *v.* INDULIN.**AZO-ERYTHRIN** *v.* ARCHIL.**AZOFLAVIN** *v.* AZO- COLOURING MATTERS.**AZOLITMIN.** A substance assumed by Kane to exist in litmus (A. 39, 25).**AZORSEILLIN** *v.* AZO- COLOURING MATTERS.**AZOPHENIN** *v.* INDULIN.**AZOPHOSPHINES** *v.* AZO- COLOURING MATTERS.**AZO-RED** *v.* AZO- COLOURING MATTERS.**AZORUBIN** *v.* AZO- COLOURING MATTERS.**AZO-VIOLET** *v.* AZO- COLOURING MATTERS.**AZOTE.** A name given to nitrogen by Lavoisier, and hence commonly used in French literature to designate that element.**AZOTOMETER.** A term applied by W. Knop to an apparatus designed to measure the nitrogen evolved by the action of sodium hypochlorite or hypobromite on ammonium salts and certain organic substances.**AZOTINE.** An explosive made in Austria-Hungary (S. C. I. 4, 366).**AZOXYBENZENE**  $C_{12}H_{10}N_2O$ . A product of the partial reduction of nitrobenzene with alco-

holic potash (Zinin, J. pr. 36, 93; Schmidt and Schultz, A. 207, 325; B. 12, 484), or with sodium amalgam containing 3·8 p.c. of sodium (Alexejeff, J. 1864, 525; Moltschanowsky, C. J. 42, 965; B. 15, 1575).

*Preparation.*—Azoxybenzene is best prepared by dissolving 1 part of sodium in 25 parts of methyl alcohol, adding 3 parts of nitrobenzene and heating for 5 to 6 hours on a water-bath in a flask provided with a reversed condenser. The methyl alcohol is then distilled off and the residue treated with water, which dissolves the sodium formate formed in the reaction, and leaves the azoxybenzene as a yellow oil; this soon solidifies, and is obtained pure by one crystallisation from alcohol (Klinger, B. 15, 866; Moltschanowsky, *l.c.* and B. 16, 81; Klinger, B. 16, 941, footnote).

Azoxybenzene or its homologues can be obtained by heating nitrobenzene or the corresponding nitro-compound with an equal weight of zinc-dust and of an aqueous solution of calcium chloride boiling at 130°; aqueous solutions of other salts may be employed, and the reaction ensues at the boiling-point of the aqueous solu-

tion (v. Dechend, Germ. pat. 43,230, February 9, 1887).

**Properties.**—Azoxybenzene crystallises in pale yellow rhombic needles, melts at  $36^{\circ}$ , and is soluble in alcohol and ether, insoluble in water. When heated with non-volatile substances, such as iron filings, it decomposes into aniline and azobenzene. Weak reducing agents, such as sodium amalgam in alcoholic solution, convert it into hydrazobenzene (Alexejeff, J. 1867, 503); but more powerful agents, such as zinc chloride in acid solution, reduce it chiefly to aniline, a small quantity of hydrazobenzene and bases derived from it by molecular changes being also formed. (Schmidt and Schultz). Azobenzene yields two isomeric nitroazoxybenzenes when heated with concentrated nitric acid (Zinin, A. 114, 217), and when heated with concentrated sulphuric acid to a moderate temperature is converted into the isomeric hydroxyazobenzene (Wallach and Kiepenheuer, B. 14, 2617).

In addition to azoxybenzene other azoxy-compounds have been prepared by reducing the corresponding nitro-derivatives either with sodium amalgam in methyl alcohol solution or with zinc-dust and soda (cf. Limpricht, B. 18, 1405; Klinger and Pitschke, B. 18, 2553; Janovsky and Reimann, B. 22, 41; v. Dechend, l.c.). The azoxy-compounds derived from metanitriline, the nitrotoluidines melting at  $78^{\circ}$  and  $107^{\circ}$ , and the nitroxyldine melting at  $123^{\circ}$

yield, when diazotised and combined with phenols, amines or their sulphonic acids, a class of yellow, orange or red azo-dyes, which can be employed for cotton and wool (Poirrier and Rosenstiehl, Germ. pat. 44,045, July 27, 1887; 44,554, September 6, 1887).

**AZOXY-COLOURING MATTERS.** The only member of this group of dyes of any importance is the sodium salt of azoxystilbene-disulphonic acid  $C_{14}H_9N_2O(SO_3Na)_2$  obtained by boiling *p*-nitrotoluene-sulphonic acid with caustic soda. Known in commerce as 'sun yellow' or 'maize.' Brown powder, soluble in water with brown-yellow colour; violet solution with sulphuric acid (Schultz a. Bender, B. 19, 3234).

**AZULIN.** Blue colouring matter, contained in certain essential oils; e.g. chamomile, millefolium, and wormwood.

**AZULINE v. AURINE.**

**AZULINE YELLOW.** A colouring matter, obtained by nitrating azuline or azuline-sulphonic acid (Machenbauer, G. P. 29,064, April 8, 1884; expired June 1885).

**AZURE v. PIGMENTS.**

**AZURIN**  $C_{15}H_{12}N_4O_3$ . Obtained by heating salicylic aldehyde with *o*-tolylenediamine. Colourless tables, giving blue fluorescent solutions (Ladenburg, B. 11, 596).

**AZURINE v. AURINE.**

**AZURITE v. LAZULITE and COPPER.**

**AZYLIN v. AZO-COLOURING MATTERS.**

## B

**BABBIT'S METAL.** An alloy of 25 parts tin, 2 parts antimony, and 0.5 part copper, used as an anti-friction metal v. ANTIMONY.

**BABLAH or WEB-NEB.** Commercial names for fruits of several species of acacia; used in the East, in combination with alumina and iron mordants, to produce various shades of drab and fawn colour in calico printing. East Indian bablah is obtained from *Acacia Bambolah*; Senegal and Egyptian bablah from *Acacia Nilotica*. The aqueous extracts contain a red colouring matter together with considerable quantities of gallic and tannic acids.

**BABUL BARK.** The bark from *Acacia arabica*, the babul tree of Bengal. Used in India as a tanning material.

**BABUL GUM.** An inferior kind of gum arabic from *Acacia arabica*. Known also as 'Bengal gum' or 'Gond babul.'

**BADAM KOHSE v. APRICOT OIL.**

**BAEL FRUIT.** The dried half-ripe fruit of *Ægle Marmelos*, from Malabar and Coromandel; is used in diarrhoea and dysentery, and the fresh pulp is sometimes employed as a laxative.

**BAKING POWDERS.** Are chiefly used as substitutes for yeast. A common form is prepared by mixing  $\frac{1}{2}$  lb. of tartaric acid with  $\frac{3}{4}$  lb. each of bicarbonate of soda and potato farina.

Delfonte's is made from  $\frac{1}{4}$  lb. tartaric acid,  $\frac{1}{2}$  lb. alum,  $\frac{3}{4}$  lb. bicarbonate of soda, 1 lb. of farina, and 3 oz. of sesquicarbonate of ammonia (Cooley's Encyclopædia, 1, 373).

Goodall's powder is a mixture of 2 parts of rice flour with 1 part of a mixture of tartaric acid and sodium bicarbonate.

Davis (Eng. pat. 1,249, 1879) prepares a powder from acid ammonium phosphate and bicarbonate.

Weitz (B. C. 1880, 389) employs phosphoric acid 5.1 grams, sodium carbonate 8.7 grams, and flour to make up to 1,000 grams.

Horsford (Eng. pat. 2,875, 1880) uses dried phosphoric acid and bicarbonate.

Avery (Am. pat. 235,615, 1880) claims the use of a mixture of acid calcium lactate and alkaline carbonates and bicarbonates.

McDonald (Eng. pat. 306, 1884) substitutes acid sulphate of potash or soda for tartaric acid or cream of tartar generally employed, the proportions suggested being 1 to 2 oz. of flour, 1 oz. of acid carbonate, and 1 to  $1\frac{1}{2}$  oz. of acid sulphate of potash or soda.

**BAKUIN.** Russian mineral machine oils; recommended for lubricating heavy machinery on account of their high viscosity and great power of resisting cold (Scifensied. Zeit. 31, 366; 32, 378; S. C. I. 3, 181).

**BAKUOL.** A name given by Mendeléeef to an illuminating oil, prepared from the crude oils of Baku by mixing ordinary kerosene of sp.gr. 0.82 to 0.83 and flashing-point  $20^{\circ}$  to  $30^{\circ}$ , with the so-called intermediate oil, which has a sp.gr. of 0.86 to 0.88 at  $15^{\circ}$ , and is not inflammable at  $100^{\circ}$ . The mixture has a sp.gr. of

0.84 to 0.85, and flashes at temperatures varying from 50° to 70°. From 100 parts crude naphtha 20 to 30 parts of kerosene and 10 to 20 parts of intermediate oil can be obtained.

The following table gives the sp.gr., flashing-point, and luminiferous value of four bakuols examined by Ilimow:

Specimen of oil	Sp.gr. at 17°C.	Flashing point at 760 mm.	Candle-power	Consumption per hour in Russian lbs.	
				For the lamp	Per candle-power
No. 1	0.8280	36°C.	7.40	0.0588	0.0080
2	0.8310	37.5	10.40	0.0633	0.0060
3	0.8360	39.5	9.84	0.0633	0.0064
4	0.8310	49.5	8.30	0.0975	0.0081

(Lit.: Mendeléef, Zeitschr. Technik, 1886, No. 109; C. Z. 1883, 231; Ilimow, C. Z. 10, 1,459; S. C. I. 2, 238; 5, 661; 6, 135) v. PETROLEUM, RUSSIAN.

**BAKURIN.** A lubricating oil, prepared by mixing 100 parts of crude Baku oil with 25 parts of castor oil and 60 to 70 parts of sulphuric acid of 66° B. After standing the mixture is stirred two or three times with water, the water run off, and the oil treated with soda or potash (Müller, G. P. 35,141, 6 Sept. 1885; D. P. J. 260, 240).

**BALANCE.** A generic term, designating a variety of machines for ascertaining the weight of a body in terms of the weight, at the time and place, of a standard mass (gram, ounce, pound, &c.), and thus determining its mass. By means of a balance and a set of 'weights,' we ascertain that a body has P times the weight of the unit piece of the set, and conclude that its mass is P times the mass of this piece likewise, whatever the chemical nature of the body may be. In justification of this inference we might refer to Newton's pendulum experiments, or to the often proved chemical axiom that the weight of any body or set of bodies is independent of the state of combination of its elements. But from the standpoint of the chemist it is sufficient to know that, supposing even each element had its own factor for converting 'weight' into mass, it would still follow that the weight of a body, however complex, is equal to the sum of the weights of what in any sense we may call its 'components,' and that the ratio of the weight  $W_1$  of a body of fixed elementary composition to the weight  $W_2$  of another body of even a different fixed composition is as constant, although perhaps not equal to the ratio of the masses  $M_1$  :  $M_2$ . Of all balances the equal-armed lever balance, often called '*the balance*' *par excellence*, is by far the most important.

The balance exists in a variety of forms, which, however, all seek to realise the same ideal machine. An absolutely rigid beam, so suspended that whilst it can rotate freely about a certain axis (which goes across it somewhere above its centre of gravity, and of which every point holds a fixed position in reference to the stand) it is not capable of any other motion. From two points, *a* and *b*, which lie in the same plane as the axis of rotation—one near the left, the other near the right end of the beam—the pans are suspended by means of absolutely

flexible linear strings. *a* and *b* are equidistant from the axis of rotation. So far all balances are alike. In now passing to the actual instrument, we shall confine ourselves in the main to the class of balances known as precision balances.

Of the difficulties involved in the construction of such balances, that of producing a sufficiently light and yet practically inflexible beam seems to have rested most heavily on the minds of the earlier makers; but there can be no doubt that many of their efforts in this direction, which occasionally resulted in what we should now call fantastical beam-forms (hollow ellipsoids, monstrous skeleton-forms, &c.), must be traced back to their inability to reach a sufficient degree of precision in the geometric adjustment of the three pivots, and to their charring against the flexibility of the beam what was really owing to these defects in the adjustment. As these difficulties were overcome, beams assumed less fantastic forms. Sacré of Brussels, we believe, never uses any but plain rod-shaped beams (only perforated in the middle to insert the bearing of the central knife). Most balance makers, however, prefer the form of a largely-perforated rhombus or isosceles triangle (cut out, virtually, of a plate of metal), and thus attain all that is needful without offending the eye by unduly stretching the middle section, and without using anything more intrinsically rigid than hammered brass or some kind of bronze. In reference to ordinary chemical balances (for charges up to say 100 grams), it would be no great exaggeration to say that any reasonably-made beam is sufficiently rigid; only in the case of balances intended for very high charges, such as 5-10 kilogrammes, is it at all worth while to employ refinedly-designed beam-forms, or to look out for a material of exceptionally high rigidity. For these particular balances hard steel would be the best material; but, unfortunately, steel beams are apt to become magnetic. With small assay-balances intended for charges up to, say, 5 grammes, on the other hand, the question of rigidity is practically out of court, and the use of an exceptionally light material—such as aluminium, or, better, that alloy of 95 parts of aluminium and 5 of silver (which Sartorius of Göttingen uses for small balances generally) is indicated.<sup>1</sup> In all balances the axis of rotation is realised in a straight knife-edge ground to a prism of hard material, which is firmly fixed to the beam, traversing it crosswise and resting on a hard bearing. In ordinary balances the middle knife is simply driven through the beam, and only its two ends are supported in cylindrical, or, what is better, roof-shaped bearings, which form secures to the edge a sufficient fixity of position, forward and back-sliding being prevented by cutting off the ends of the knife obliquely, so that the edge terminates in two points, and closing the bearing at each end by a steel plate so that the knife has just room between without jamming. In suspended balances the central bearing is fixed at the lower end of a light framework, terminating above in a hinged-on ring for suspending the instrument from a fixed hook or the thumb of the operator.

<sup>1</sup> For a fuller discussion of this subject v. the writer's Memoir (Bib. 6, p. 322).



In all precision balances the central bearing is attached to a fixed pillar, and is plane; in the best balances the bearing is made of one piece, and the central knife-edge rests upon it in its entire length. A plane bearing necessarily involves an arrestment so constructed that, besides doing its primary duty, it assigns to each point of the central knife-edge a fixed position on its bearing. In former times hard steel was used exclusively for both knives and bearings; subsequently agate bearings came to be combined with steel knives. Robinson of London was the first to make both knives and bearings of agate. The agate knife adds nothing to the precision of a newly-made balance, but it always remains clean, while a steel knife, in a chemical laboratory more especially, is apt to rust. Steel knife-edges are generally ground to an angle of  $60^\circ$  (or  $90^\circ$  for very heavy charges). In agate knives, as made by Oertling, only the body of the agate prism is ground to  $60^\circ$ , while the edge is formed by two narrow facets, inclined to each other at a far more obtuse angle. Such an obtuse edge stands many years' constant use without wearing out. Quite lately an American maker has introduced the artificially made osmium-iridium, which is used for the tipping of stylograph pens, as a material for both knives and bearings.

For the realisation of the two point-pivots A and B, a great many combinations have been invented. A now obsolete construction of Weber's (Bib. 2) adapts itself very closely to our ideal conception. He provides the beam at its two ends with knife-edges turned sideways and suspends the pans by means of threads of unspun silk which are fixed somewhere in the back of the beam and hang over the edge. The axis of rotation is realised similarly. In ordinary balances, as a rule, a vertical slit is cut into each end of the beam, and this is traversed by a short prismatic knife, the edge of which is a circular arc of small radius which stands perpendicular to the line A B. From each such knife the pan is suspended by means of an 8 or 2-shaped steel hook. This construction, if well executed, may afford high precision, but the suspender-hook is apt to rub against the sides of the slit in the beam. Hence, wherever the hook-and-eye arrangement is adopted for precision balances, it is modified in this sense, that the knife-edge forms a circle of relatively large radius which lies entirely outside the body of the beam. This system, compared with those considered in the sequel, offers the advantage of easy adjustment. It used to be very popular with balance-makers, and many excellent instruments have been produced with it especially by Deleuil of Paris. For small assay-balances it is indeed probably as good as any other that could be named; for balances intended for higher charges it does not possess sufficient durability, although, as the writer is able to say from his own experience, if well made, it lasts better than is generally supposed. In modern balances it is rarely seen; in these, as a rule, the pans are suspended from long straight knife-edges, similar to the central one, by means of broad bearings which, of course, must be arranged so that they neither twist nor slide. A very efficient and easily-made arrangement is to give the bearing the form of a roof

cut and of one side of a prismatic block of steel or agate, and to fix it to the upper end of a stirrup-shaped or J-shaped holder which terminates below in an eye, from which the pan is suspended by a suitable hook. The eye stands at right angles to the knife-edge; its working point, when the instrument is in use, lies vertically below the centre of the respective end-edge, and the effect is the same as if the whole of the load were concentrated in that one centre-point, although the pressure of the bearing on the knife is equally distributed over the whole of its working length. This hook-and-eye arrangement is absolutely indispensable if the pans are suspended by stiff stirrups, because, if these were rigidly connected with their bearings, the virtual point of application of the load would shift forwards and backwards on the edge, and the least want of parallelism between it and the axis of rotation would cause the balance to give inconstant readings.

These roof-shaped bearings, until some 10 or 15 years ago, were used almost exclusively by all German makers, although an undoubtedly superior system had been introduced successfully by Robinson of London many years before. In it the pans are suspended by *plane* bearings which a suitable extension of the arrestment keeps in their right positions. Robinson's balances were justly famous in Great Britain—a few of them are still working to this day—yet, after Robinson's death, Oertling was almost the only balance-maker who followed him in this respect. The general plea against the system was that flat end-bearings were liable to twist; and some, after having adopted Robinson's plan, 'improved' upon it by cutting out a central portion of each end-knife, so that it worked only with its two ends; proving thereby that they did not understand their business, because a *really plane* bearing, as a matter of fact, does *not* twist on a *really straight* knife-edge, even if the pan oscillates strongly. The principal advantage of the Robinson system is that it enables one to do what the roof-shaped bearing prohibits, namely, to satisfy himself that the knives and bearings are geometrically perfect. But here, as in all analogous cases, we must not forget that the excellence of an instrument—supposing it to be based on a reasonable system—depends far more on the skill of the maker than on the theoretical perfection of the design.

From the bare realisation of the ideal machine, we now pass to the accessories which a balance needs in order to become a convenient instrument, and we will consider these in the order of their importance.

The *arrestment* is a mechanical contrivance to enable the beam to be arrested at any point of its angular motion, and to bring it to permanent rest in its '*normal*' position, in which the plane of three axes stands horizontal. If the three pivots are self-adjusting, there is, strictly speaking, no need of an arrestment; still for the rapid execution of precise weighings it is almost indispensable.

If the central bearing forms part of a suspended frame, an arrestment is easily devised in the ways illustrated by figures 1 and 2. Fig. 1 explains itself; in fig. 2 the balance is hinged on to the bent-down end of a flat bar which slides

up and down in guides fixed to the pillar between two beds of rollers  $2 \times 2$  in the guides on the front side of the bar, and one which is pressed against its back by a spring. At its lower end the bar has a small wheel which rests on the

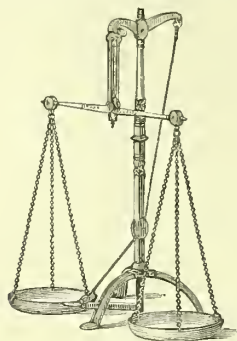


FIG. 1.

shorter end of the hinged lever by means of which the balance is raised or lowered. A small vertical adjusting screw below the shorter end of the lever defines the lowest position of the bar at which the pans just touch the table without slackening the chains. In either case it is an improvement to suspend a heavy block of metal at the lower end of the frame, to compel it to hang plumb, and to hinder it from oscillating. The specific advantage of *suspended* balances is that they need no horizontal table or levelling screws at the board on which they may be erected. But pillar-balances are on the whole more convenient. In the case of these (supposing plane bearings to be absent) a good system is to fix

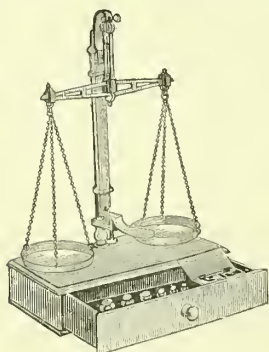


FIG. 2.

the central bearing to the top of a rod which slides up and down within the pillar—properly guided to prevent shaking and rotatory motion—and, with its lower end, rests on an eccentric concealed in the sole and governed by a lever- or disc-shaped handle. The eccentric must be so adjusted that when it is at one of its extreme positions, the pans just touch the board and no more, while, when it is in its other extreme position, the beam is at its maximum angle of free play. In the excellent *Tarirwaagen* of

Messrs. Becker's Sons, Rotterdam, this system of arrestment is realised to perfection.

The system need only be slightly modified to adapt itself to the case of a plane central bearing, but we prefer to at once pass to the case of *three* plane bearings, and in doing so cannot do better than describe a balance (for charges up to 5 kilos.) which Mr. Oerling made for us some years ago. As shown by fig. 3, the instrument rests

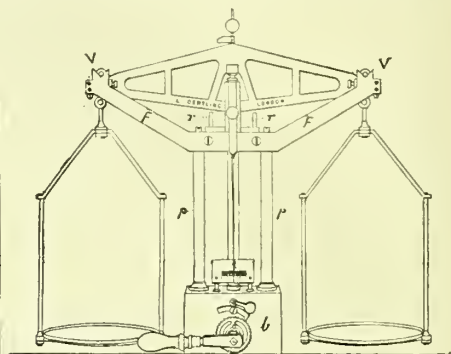


FIG. 3.

on three pillars standing on a hollow square block of iron which conceals the eccentric. Firmly fixed to the top ends of the pillars is a substantial brass frame which terminates at its two ends in V-shaped supports for the end-bearings. These latter are agate plates cemented each to the horizontal bar of a kind of stirrup, the bar terminating on each side in a cylindrical steel pin which, when the balance is at rest, lies in the corresponding V of the frame. The central pillar conceals a movable steel rod, provided at its lower end with a wheel which rests on the eccentric. Its upper end carries a substantial brass block which divides into two short piers above, whilst it expands below into a horizontal plate, pierced by a circular perforation near each end. These perforations fit exactly around two cylindrical steel pins, *r*, *r*, fixed to the top plate of the pillars, so that the rod, when moving up or down, cannot turn or shake in the slightest degree. The space between the two piers is bridged over by the central bearing, a plane agate plate fixed to a prismatic piece of brass, which is dovetailed into the tops of the piers, so that, while perfectly steady when in its place, it can without much effort be slid out or in (fig. 4). It is inserted while the beam is being held in its intended position and passes through a large perforation in the beam into which the middle knife projects. The beam terminates at its left end in one, at its right end in two, horizontal steel pins whose shoulders are continuous but rapidly expanding surfaces of rotation, and these pins fit, the single one into a notch, the couple into a fork, forming part of the fixed arrestment-frame. In the arrested balance each bearing is almost in contact with its knife; if the eccentric be now turned, the central bearing rises and lifts the whole, beams and end-bearings, to a greater or less height, and ultimately into that maximum height at which the eccentric stands still without

being *held* in its position. If the eccentric be now turned the other way, both the beam and the end-bearings fall back, ultimately, into their prescribed positions of rest, even if they should have twisted, which, however, they never do in the instrument under description. For a balance intended for quick work, and more especially for one used occasionally for the weighing out of predetermined quantities of solids or liquids, this system

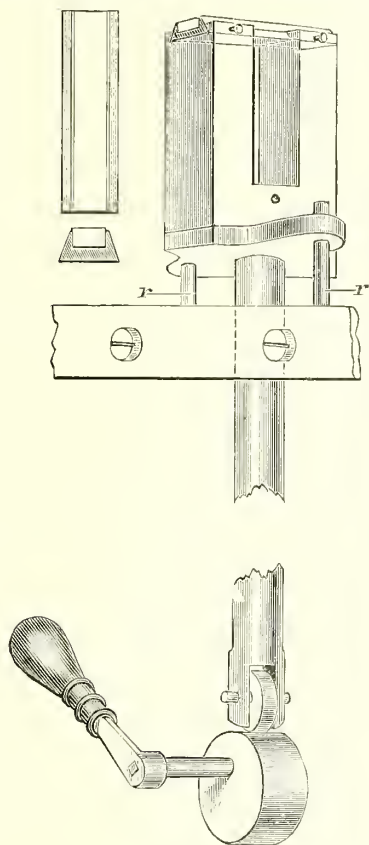
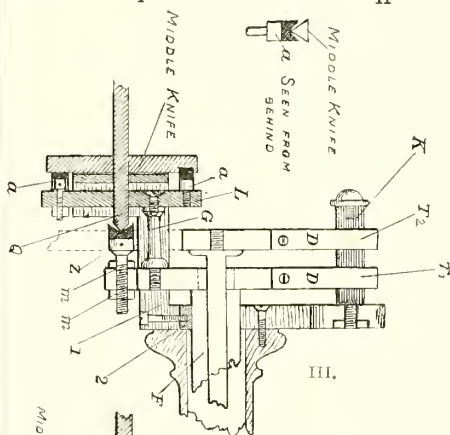
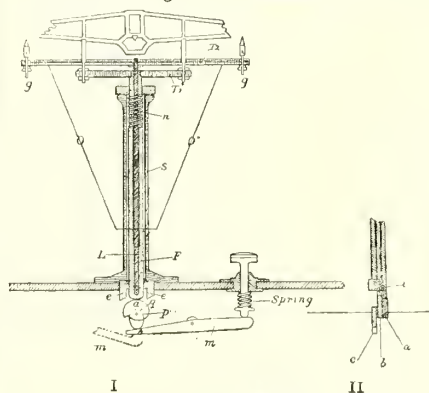


FIG. 4.

of arrestment is the best that we know of, because it enables the instrument to be handled pretty much like an ordinary pair of scales; only, to be able to do so to the best advantage, and without spoiling the terminal pivots, the pans must be suspended by flexible short-linked chains whose length is so adjusted that the pans just touch the table when the balance is fully arrested. Stirrup-shaped pan-suspenders (as represented in the figure) are more convenient than chains in many respects, but, for the purpose under consideration, they do not work with plane end-bearings. The ratchet-wheel visible in the figure was intended to enable the eccentric to be arrested at intermediate positions (in taring with garnets and similar operations) but was found not to work satisfactorily; it is simpler and better to have a block of wood so adjusted that when put under the handle it just raises the beam suf-

ficiently to enable one to see which side goes down.

Instead of fixing the arrestment-frame to the



III. Section through pillar and middle knife;  
IV. Horizontal projection.

FIG. 5.

pillar and making the central bearing movable, we may of course do the reverse, and this latter system, indeed, is generally preferred for precision balances of a higher order.



The kindness of Messrs. C. Standinger's Nachfolger, of Giessen, Germany, enables us to give a detailed description and drawing of the kind of movable frame-arrestment which they are in the habit of applying to their best instruments.

As shown by fig. 5 (I. to IV.) the pillar is hollow and accommodates a round bronze rod  $r$ . This rod itself, however, conceals a co-axial round rod  $l$  of nickelled steel. The bronze rod  $r$ , at its lower end, is guided by perforated blocks,  $e$ ,  $e$ , fig. I., while at its upper end it terminates in a thinner cylinder surrounded by a gently acting spiral spring  $n$ . The head of the pillar is perforated and guides the attenuated end of  $r$  in its up-and-down motion. The inner (steel) rod,  $l$ , is guided similarly within the bronze rod  $r$  and has a spring  $i$ , fig. II., about its lower end to assist its natural tendency to sink. The two rods  $r$  and  $l$  carry two independent arrestment-bars;  $l$  the bar  $\tau_2$  for the end-bearings,  $r$  the bar  $\tau_1$  for the beam.

A square pillar  $\kappa$  (figs. III. and IV.), which rises from a prolongation of the head of the stand pillar  $s$ , by passing through perforations in the two bars  $\tau_1$  and  $\tau_2$ , prevents any motion of these about the axis of their rods. As shown by fig. IV., an adjusting screw, passing through the bar, and a flat spring  $t$  on one side of the square perforation of the bar ( $\tau_1$  or  $\tau_2$ ) enforce steadiness of motion.

The upright pins  $g$   $g$  (I.), which are tipped with sharp agate cones, arrest the end-bearings by rising into corresponding conical hollows in the latter. (Fig. 5, though taken from an Oertling

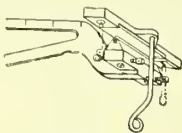


FIG. 6.

balance, will give an idea of the way in which these pins work.) The two slanting lines  $O$   $O$  (fig. I.) are meant to indicate two supports, which pass through slots in the pillar  $s$  and the bronze rod  $r$ , and are fixed to the inner rod  $l$ , to lend additional rigidity and steadiness of motion to the end-bearings arrestment.

The arrestment of the beam is effected by two adjustable piers  $z$  rising from the bar  $\tau_1$  of the bronze rod. The tops of these piers carry roof-shaped agate bearings, in which the arrested beam lies with its lower (bevelled) edge. This would be sufficient to keep the beam from turning. To hinder it from moving progressively, there is a horizontal frame  $u$  (figs. III. and IV.) united with bar  $\tau_1$  by two little pillars  $g$   $g$ , and carrying two agate bearings, a roof-shaped one at the hind end and a plane one at the front end of the middle (agate) knife. The roof-shaped bearing receives that end of the middle knife as the roof-shaped bearing of an ordinary balance would (so that by it, and the two beam-supports, three points of the arrested beam are fixed in prescribed positions); the plane bearing in front only supports the knife as it rises up to it on arresting. This plane bearing is adjustable

by means of a screw, so that the arrested central knife-edge can be made rigorously parallel to the fixed central bearing of the working instrument.

There are three eccentrics, all attached to the same axis and governed by the same handle (fig. II.) one,  $a$ , for the bronze rod  $r$ , a second,  $b$ , for the inner steel rod  $l$ , and a third  $c$  for a pan-arrestment, whose mode of acting will readily be seen by a glance at fig. I. When the handle stands so that line  $p$  (fig. I.) is vertical, the beam is arrested; after this point has been passed, the beam-supports remain at the same altitude, but, on turning the handle further, bar  $\tau_2$  is raised to lift the terminal bearings as soon as line  $q$  stands vertical. The last third of the motion of the handle arrests the pans.

The principal feature in Messrs. Staudinger's Nachfolger's arrestment obviously is the relative independence of the beam-arrestment and of the end-bearings arrestment of one another. In most other movable frame systems there is only one frame for both, and things are arranged so that the middle edge is held fast after the end-bearings have been lifted by a hair's breadth, and that the upward motion comes to an end as soon as the middle knife is just visibly above its bearing. A refinement upon this construction is to merely effect the three contacts, and then, by means of a special eccentric, to let the middle bearing drop through a distance of 0.1 or 0.2 mm.

Whilst all the several points of a rigid though movable arrestment-bar move up and down in vertical straight lines, the end-edges of the vibrating beam describe circular arcs. Hence whenever the bar is raised against the *slanting* beam, the end-bearings *tend* to slide over their knives and to spoil them. To preclude the possibility of this, Becker & Sons, in their finest balances, make the bar for the end-bearings arrestment of two halves which are hinged on to the pillar in or very near the axis of rotation. Sartorius adopted this system and brought it into a slightly different form, regarding which we refer to Bibl. 4, where it is illustrated by a drawing.

In a balance which has only plane bearings, no kind of arrestment, of course, will give satisfaction, unless its several parts, and also the pillar and the sole, are sufficiently substantial to ensure absolute constancy of configuration and absolute steadiness of motion even after long-continued use. The old masters used to pay great attention to this important point, but it is sadly neglected by the majority of their present successors.

In a balance of which the end-pivots are self-adjusting, the movable arrestment frame assumes a very simple form. All that is needed is a small frame bearing V-shaped notches for arresting the middle knife in a prescribed position, and fixed to a horizontal bar with two projecting pins, in order, at the same time, to support the beam in a horizontal position. As these pins have no other function, the bar may be very light, and the whole system need not have that absolute steadiness of motion which is indispensable in the case of plane end-bearings.

The needle and scale serve to define the angular position of the beam. In all modern precision balances the needle points downwards, and is meant to embody a straight line passing

through the axis of rotation and standing perpendicular on the line connecting the two point pivots A and B. The scale is attached to the pillar; its zero, if the stand is properly levelled, lies vertically below the axis of rotation. To enable the stand to be levelled, there must be either a plumb line or two spirit levels *fixed to the pillar*, and so adjusted that when they point to their zeros, the line connecting the zero of the scale with its projection on the middle edge is vertical. The scale should be so graduated that the needle-line, if produced, would cut, not the circle described by the needle's reference point, but the horizontal tangent to this circle, into pieces of equal length (*v. infra*). In most practical cases, however, this comes to the same as saying 'into pieces of equal angular value.' In balances provided with a fixed arrestment frame the scale should be made to move up and down with the beam, so that its position in reference to the needle remains constant. In most balances the end-point of the needle is just clear of the upper circular edge of the scale, but it is better to make its lowest portion almost linear, and let this project over the scale and almost touch it.

*The rider.*—Small weights are difficult to handle and easily lost. To avoid this inconvenience, Berzelius conceived the happy idea of dividing the right side of the beam, or rather the horizontal lever arm corresponding to it, into ten equal parts, and substituting one rider weighing ten centigrams for all the centigram and milligram pieces of the set of weights. Obviously the rider, when suspended at the first, second, &c. mark from the centre, acts like 1, 2, &c. centigrams placed in the pan, and it is equally obvious that every tenth of a division on the beam corresponds to one milligram of additional weight. This system was universally adopted and is still in use, only with this qualification, that we now apply it to the counting of the milligrams by means of a rider weighing ten milligrams. The reason for the change is obvious. In most balances the points 0 and 10 of the rider-scale are inaccessible. Messrs. Becker's Sons avoid this inconvenience by dividing the arm into twelve parts, and supplying a rider weighing twelve milligrams. Other makers, for instance Messrs. Verbeck & Peckholdt, of Dresden, make the top bar of their beams exactly horizontal, and, besides keeping it clear of impediments, make it project beyond the terminal edges. One of the advantages of this system is that, in the case of a short beam, it enables us to double the degrees of the rider scale, by dividing each arm into only five (integer) parts, numbering these from the left knife onwards and using a rider weighing five milligrams. Only, if we do so, the rider suspended at the zero must be counted part and parcel of the instrument. Bunge provides a special rider-bar so contrived that the path of the rider lies in the plane of the three axes. This, *theoretically*, is the most perfect arrangement.

A rider arrangement, to be complete, must be supplemented by a mechanical contrivance enabling one to shift the rider while the balance case is closed, and to do so with greater rapidity, ease, and certainty than would be afforded by a forceps, supposing the case to be open. Rider-guides fulfilling this latter condition are scarce;

even with the best the rider drops down occasionally, and has to be searched for.

To avoid this source of annoyance Hempel does away with the rider and substitutes for it a

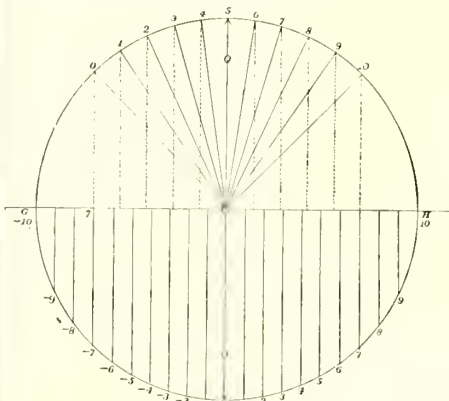


Fig. 7.

vane with a limb graduated into milligrams (*v. infra*).

*The gravity bob*—a small button or disc of metal so attached to a wire standing vertically on the top of the beam exactly above the axis of rotation that it can be screwed up and down along the whole range of the wire. It enables one to raise or lower the centre of gravity of the beam, and thus to establish any desirable degree of sensibility.

A bob thus constructed meets all the requirements of the balance-maker, but for the chemist who uses the balance it is desirable to have an arrangement which enables him at a moment's notice to establish any predetermined degree of sensibility. Such an arrangement was invented by the writer some years ago (Bibl. 8 and 5). It consists of a small bob fixed by mere friction to the upper end of the needle, which at that part has the form of a triangular prism, and is provided with a graduation. The mode of standardising the scale is explained below.

*Some arrangement for establishing perfect equilibrium* in the unloaded instrument is required. A small bob screwing along a horizontal wire fixed to some convenient part of the beam answers best. Less convenient is a 'vane,' meaning a little movable horizontal lever attached to the lowest point of the wire, which carries the ordinary gravity-bob, or to the upper part of the needle. To understand the working of the vane—and at the same time that of Hempel's invention above referred to—substitute for the vane an equivalent rigid line (fig. 7). If the vane-line stands in the position O o—*i.e.*, if it is parallel to the middle knife, it adds no weight to either side, if turned through 90° into position O (10), it virtually adds, let us say, 10 milligrams to the charge of the right pan. Divide the line O (10) into ten equal parts, erect an ordinate at each point, and you find the points 0, 1, 2, 3, &c., of the circular path of the end-point of the vane, to which the vane-line must point, if the virtual addition to the right pan is to be equal to 0, 1, 2, . . . 10 milligrams. A glance

at the figure shows one weak point in the vane contrivance. There is, however, no need of our dividing the circular limb exactly in the way of our figure. We may, for instance, place the zero at the  $-7$  and the ten at the  $+7$  of our figure, divide the interval between the projections on line (10) (10) of  $+7$  and  $-7$  into ten equal parts, and so adjust the mass of the vane and its distribution that, by turning it from the new zero (at  $-7$ ) to the new '10' (at  $+7$ ), we virtually add 10 milligrams to the right charge. The degrees, corresponding each to 1 milligram, then become so nearly equal to one another that the subdivision of each into ten parts of equal angular value is permissible.

### THE THEORY OF THE BALANCE.

For a first approximation imagine a balance which is ideally perfect, and assume it to be charged with  $P$  grams from the left and with  $P$  grams from the right point pivot. The balance, when free to vibrate, can remain at rest in only its normal position, and if brought out of it will vibrate about it as a pendulum, because the two charges are equivalent statically to one heavy particle weighing  $2P$ , situated in the central knife-edge. Now, put a small overweight  $\Delta$  on, say, the right pan; the position of potential rest will shift, and the beam, to reach it, must turn (downwards on the right side) through a certain angle  $\alpha$ , which depends only on  $\Delta$  and on the weight  $W$  of the empty beam, which latter we may assume to be concentrated in its centre of gravity  $c$ , the force  $2P$  being obviously out of consideration. But the two weights,  $\Delta$  at  $b$  and  $W$  at  $c$ , are equivalent to a point weighing  $W + \Delta$  and lying on the straight line  $c b$  at a point  $c'$ , not far from  $c$ . The new position of rest is gained as soon as  $c'$  lies vertically below the axis of rotation, or, to put it in other words, the right side of the beam goes down until the leverage of  $\Delta$  is so far reduced and that of  $W$  has so far increased, that the two *momenta statica* are equal to each other.

Imagine now the axis of rotation were shifted vertically upwards through a small height  $h$ , but remained parallel to itself. The imaginary point weighing  $2P$  now, as soon as the beam turns, has a lever and helps the weight  $W$ ; the beam will turn through a less angle  $\alpha'$  to gain its new position of rest, and, supposing  $2P$  to increase,  $\alpha'$  becomes less as  $2P$  increases.

Imagine now the axis of rotation to be shifted downwards towards the centre of gravity. The heavy point weighing  $2P$  grams now helps  $\Delta$ , and the angle which separates the two positions of rest will become greater than the original angle; the greater  $2P$  the greater will be the actual angle  $\alpha''$ . But the two weights,  $W$  concentrated in  $c$ , and  $2P$  concentrated in the centre of the line  $a b$ , taken jointly, are equivalent to one point  $c'$  weighing  $W + 2P$  grams, and situated on the straight line connecting the two points; and supposing  $2P$  to increase gradually from *nil* onwards,  $c'$ , in the second case, will rise and rise, and at a certain value of  $2P$  fall into the axis of rotation. The balance then has no definite position of rest; and if  $c'$  rises still higher, the balance upsets. However small an overweight  $\Delta$  may be put on either side, the

beam would have to turn upside down to reach its one (theoretical) position of stable equilibrium.

The balance-maker of course takes care so to adjust his instrument that even if the sensibility is at the highest value which the balance is meant to afford, and the two-sided charge  $2P$  at its maximum likewise, the centre of gravity of the whole system lies on the safe side of the axis of rotation.

Assuming this condition to be fulfilled, the balance to be exactly equal armed and to be charged with a pan weighing  $p_0$  grams and a load of  $p$  grams on each side, the angle  $\alpha$  of deviation is governed by the equation

$$tga = \frac{\Delta l}{Ws + 2(P_0 + p)h}, \quad (1)$$

where  $l$  stands for the arm-length,  $s$  for the distance of the centre of gravity of the empty beam from the axis of rotation, and  $h$  for the distance of the axis of rotation from the plane of the two end-edges, the axis being assumed to lie *above* the plane. In the opposite case  $h$  must be assumed to be negative, or the *plus* sign before the second term in the denominator be replaced by a *minus* sign. But  $tga$  is the ratio of the absolute length of scale (measured tangentially, *v. supra*) corresponding to angle  $\alpha$  to the distance  $l$  of the tangent-zero from the axis of rotation. Hence we have

$$n = \frac{\Delta l}{Ws + 2(p_0 + p)h} = \Delta \cdot 'E' \quad (2)$$

Where, supposing  $l$  to be measured in tangential scale-degrees,  $n$  may be read as meaning the number of degrees through which the needle turns in consequence of the addition of  $\Delta$ . The product condensed into ' $E$ ' we will call the 'sensibility.'

The reciprocal of  $E$ , *i.e.* the number  $E^{-1} = \frac{1}{E}$ , is the weight-value of 1 degree of the scale—*i.e.* the particular  $\Delta$  which makes  $n=1$ . With a precision balance the milligram is a convenient unit for  $\Delta$ .

For a balance provided with the writer's auxiliary bob, eq. (2) may conveniently be brought into the form

$$\frac{\Delta}{n} = E^{-1} = \frac{(Ws + 2Ph) + b(y_0 + y)}{lI} \quad (3a)$$

Where  $b$  is the weight of the bob and  $y_0 + y$  the distance of its centre of gravity from the axis of rotation  $y_0$ , being that distance which prevails when the bob is at its highest (zero) position. In a well-made balance the influence of  $P$  on  $E$  is small; we may therefore assume the  $P$  of the equation to be some average value, and, contracting constants, say, the weight-value of one degree is

$$E^{-1} = A + By \quad (3)$$

where  $A$  and  $B$  are constants;  $A$  obviously being that value which  $E^{-1}$  assumes when  $y=0$ .  $-B$  is easily determined by one trial at  $y$  to its maximum, and the scale thus standardised.

The theory of the rider might be allowed to take care of itself if it were a general practice to place the rider's path exactly into the plane of the three axes. But such is not the case; this path, as a rule, lies above the plane, and each mark at its own altitude  $H$ . Let us therefore assume that, after the balance had been charged with  $P$  on each side, a rider weighing



$p$  had been suspended at a point of the beam corresponding to the fraction  $kl$  of the arm-length (at the  $(10k)^{\text{th}}$  mark counting from the centre). If the beam stand horizontal, and a weight  $kp$  be placed in the opposite pan, the beam will remain in equilibrium, because we have  $l(pk) = p(kl)$  whatever  $H$  may be; the rider where it is and the charge  $kp$  (virtually) in the left knife-edge are conjointly equivalent to a fixed point weighing  $kp + p$ , and situated on the straight line joining the left edge and the point  $(10k)^{\text{th}}$  where the rider is. And this equivalence holds for the slanting beam as well, and is independent of  $P$ . But the sensibility of the beam with the rider on is evidently greater than it was with the rider off. Statically speaking, the weight of the beam and the two charges  $P$  and  $P$  are equivalent to a fixed point  $C_0$  weighing  $W' = W + 2P$ , and situated vertically below the axis of rotation at a distance  $S_0$ , and this particle, conjointly with the one embodied in the rider, is equivalent to a point weighing  $W + 2P + p$ , and situated on the straight line between  $C_0$  and the point where the rider sits. Referring to a system of rectangular co-ordinates whose X-axis passes through the centre of the central edge and is parallel to AB, and whose Y-axis passes through the same centre, we have for the position of the resultant point the equations

$$x(W' + p) = lkp; \text{ and } y(W' + p) = W's_0 - pH \\ \therefore \frac{x}{y} = tga = kp \left\{ \frac{l}{W's_0 - pH} \right\} \quad (4)$$

We see that if  $H$  be constant—i.e. if the rider-path be parallel to the plane of the three axes— $tga$  is proportional to the overweight  $kp$  virtually added to the charge of the right pan; but it is as well to notice that the  $tga$  of our equation is different from the  $(tga)_0$  which is brought about if, instead of hanging the rider on the  $(10k)^{\text{th}}$  mark, we actually put  $kp$  units into the right pan. Obviously

$$(tga)_0 = (kp) \frac{l}{W's_0} \text{ and less than } tga \quad (5)$$

With a rider weighing only 10 milligrams, and, say, a hectogram balance, the term  $pH$  in the denominator comes to very little, but with a rider of ten times the weight it (as a rule) can no longer be neglected; such a rider cannot conveniently be used unless  $H$  is constant and the rider must always hang at the balance (at its zero, over, say, the central knife when it is not used as a weight), or else the sensibility has one value with the heavy rider on and another with the rider off. Another requisite is that notches cut into the beam be substituted for mere marks, and that the rider have a sharp edge to give sufficient constancy of position to its point of application.

From what we have said so far, it would appear that in a balance provided with a gravity-bob we can give the sensibility any value we may fancy. And so we can, but it does not follow that we can command any desired degree of *precision*. Because the three edges and bearings are not what they ought to be, and, as a little reflection shows, the effect of their defects is the same as if, say, the length of the right arm, instead of being at the

constant value  $l$ , oscillated irregularly between  $l - \lambda$  and  $l + \lambda$ , where  $\lambda$  is a very small length, which increases when  $W$  and  $P$  increase, but is independent of  $l$ . And this again is the same as if  $\lambda$  were *nil*, but the charge of, say, the right side, instead of being at a constant value  $P$ , varied irregularly from  $P - \epsilon$  to  $P + \epsilon$ . In a given balance charged with a given  $P$  at each side  $\epsilon$  is constant, but the corresponding angle of deviation  $\beta$  varies when the sensibility varies. Within this angle  $\beta$  the balance is, so to say, in a state of indifferent equilibrium. By going a little more deeply into the matter we easily satisfy ourselves that, even allowing for the fact that we cannot substitute a longer for a shorter beam without increasing the beam-weight,  $\epsilon$  will increase when  $l$  becomes less. In a balance meant to afford a certain degree of precision, we cannot allow the arm-length to fall below a certain (very uncertain) value  $l_0$ .

A glance at eq. (2) would show, if it were not clear without it, that, if the three axes lie in exactly the same plane—i.e. if  $h = 0$ —the sensibility becomes independent of the charge, which is a great convenience. But  $h$  obviously cannot be equal to *nil* at all charges; hence in the case of the best instruments it is regulated so that it has a small negative value when only the pans are suspended, and, by the unavoidable deflection of the beam, becomes *nil* at some suitably selected medium charge, so that, from this charge upwards, it has small positive values. That such a degree of precision cannot be attained by purely constructive methods goes without saying; indeed, any precision balance requires to be '*adjusted*' before it is fit to be used. For this purpose the value of the  $h$  corresponding to the medium charge and the ratio of the actual arm-lengths  $l':l''$  must be deter-

mined and the errors  $h$  and  $\frac{l'}{l''} - 1$  corrected.

For the direct geometric measurement of  $h$  special apparatus have been constructed, which, in their present form, we believe, afford a sufficient degree of precision; but the final test always is (or at least was until lately) at a suitable position of the bob, to determine the weight-value  $E^{-1}$  of one degree of deviation for a series of charges, say,  $p = 0, 50, 100$  grams, &c., up to the maximum charge which the balance is intended to measure; and to at least *virtually* calculate the corresponding values  $h$  by means of eq. (2). Whether  $h$  is positive or negative, is of course seen from the values  $E^{-1}$  without calculation. Supposing now  $h$  has a greater value than can be tolerated, one of the knives must be lowered or raised until at a certain medium charge the three edges are as exactly as possible in one plane. Most mechanicians provide adjusting screws for this purpose which enable one to work in a systematic manner. Some, however (for instance, Messrs. Becker's Sons, following the example of Deleuil), prefer to fix all the knives definitely and to alter the *form of the beam itself* by means of the hammer. If the central edge has to be lowered, the lower bar of the beam is struck (on both sides); if it is to be raised, the upper bar is struck, until the correction is presumably almost but not quite completely effected. The values  $E^{-1}$  are then

again determined, and if they are not sufficiently near one another, the hammering is renewed until the adjustment is perfect. In a similar manner (or by means of adjusting screws) the two arms are made equal to each other. The test here is very simple. The balance, after having been brought to the highest degree of sensibility which it will stand at the highest charge  $P$ , is charged with *exactly*  $P$  grams on each side. The longer arm goes down, and by determining the small overweight which must be added to the other side to establish equilibrium, we can easily determine the ratio  $l:l''$  numerically. All these adjustments are effected by the mechanician, and when once effected are final. Some mechanicians—for instance, the Becker's Sons—fix even the centre of gravity, but this is a mistake. A balance, to be complete, *must* have a movable 'bob' to enable the operator to give the sensibility that value which suits him best. What degree of sensibility should we choose? Answer: In general, the lowest degree which suffices for the purpose in hand. Supposing, for instance, we can neglect the half-milligram, it is of no use to screw up the bob any higher than necessary for rendering the angle of deviation corresponding to 0.5 milligram conveniently visible and no more, because the less the sensibility, the greater the range of weights determinable by the method of vibration, the greater, as is easily shown from eq. (2), the relative independence of the sensibility from the charge, and last, not least, the less the time of vibration. The time of vibration can of course not be allowed to fall below a certain minimum, or else the centres of gravity of the charges will not be able to follow the oscillations of the beam with sufficient promptitude. But this clause, with larger balances wrought at high precision, usually takes care of itself. The exact relation in a balance between the time of vibration  $t$  (in seconds) and the sensibility  $E$  is given by equation:

$$t^2 = \frac{l}{Rl} \{ k W + 2P \} . E \quad . \quad . \quad (6)$$

where  $R$  is the length of the mathematical pendulum beating seconds at the place of observation,  $P$  the total charge on one side, and  $k$  a numerical factor,  $k W l^2$  being the *momentum inertia* of the empty beam. With the customary perforated rhombus or triangle,  $k$  is very nearly equal to  $\frac{1}{3}$ . From the equation we clearly see that with a 'bob' of sufficient range we can choose our own time of vibration or our own sensibility, but we cannot choose both, in a ready-made balance. It stands differently with a *balance to be constructed*. To avoid indefiniteness, let us assume that we wished to design a balance for weighing quantities up to 100 grams with a toleration of 0.1 mgr. Let us assume also that we had made up our minds regarding the material and the general form for the beam, and that we had defined the latter so that the relation between arm-length  $l$ , and weight  $W$ , were in accordance with an equation of the form

$$W = C + B l \quad . \quad . \quad . \quad (7)$$


where  $W$  includes the empty pans,  $C$  designates the conjoint weight of all that which is independent of  $l$ ; and  $B$  stands for the weight of the

rest if the arm-length  $l = 1$ . Our equation now assumes this form

$$t^2 = \frac{l}{Rl} \{ C + 2p + b l \} E, \quad . \quad . \quad . \quad (8)$$

where  $p$  stands for the charge in each pan. This equation affords some guidance in the selection of  $l$ . Assuming for  $E$  a value which renders the decimilligram just visible, and taking  $p = 0$ , we substitute for  $t$  the smallest admissible value and solve our equation in regard to  $l$ . Of course  $l$  cannot be allowed to fall below that minimum  $l$  (*v. supra*) at which the inherent error would rise to anything like 0.1 mgr. Where does this limit value  $l_0$  lie? Staudinger used to draw the line at 200, Oertling at 180 millimetres, and similar values were adopted by other makers, until Bunge, some twenty-five years ago, showed in the most direct manner possible that a sufficient degree of constancy can be attained with an arm-length of as little as 60 millimetres. Thanks to the general excellence of Bunge's work his short beams soon became very popular with chemists, and the fact that almost all other German makers have since come to adopt the Bunge system shows that the additional perfection in the pivots which the short beam undoubtedly demands is not so difficult to realise as an outsider might be inclined to think. *Assuming this difficulty to be overcome*, it cannot be denied that the short in opposition to the long beam does offer certain advantages. 1st. It is relatively light, and hence the working of the arrestment is a less effort. 2nd. It is less liable to irregularities through one-sided elevation of temperature. Perhaps we may add that, 3rd, it is easier in its case than in that of the long beam to make a smooth-working arrestment, and on this account chiefly it enables one to weigh more quickly. 4th, and *least* in our opinion, it vibrates more quickly. Not that we value this last advantage at nothing. The writer's auxiliary bob indeed was invented with the very object of remedying the corresponding defect in the older form of the instrument, being originally intended to be used thus. In the outset, place the bob far down, say to the mark where  $1^\circ$  of deviation corresponds to 2 mgrs. or some other value securing great rapidity of vibration, and establish equilibrium as far as thus possible. Then raise the bob to the mark at which  $1^\circ = 0.1$  mgr., allow to vibrate, shift the rider correspondingly, and verify your result. The writer, however, soon came to find this method less convenient than he had expected, and adopted another very obvious expedient. It is easy in any beam to bring down the time of vibration to the least value one could reasonably wish for by screwing down the bob to the corresponding place. This, of course, may render the decimilligram invisible to the naked eye. But why not help the eye by optical means? An ordinary lens magnifying six times linearly affords more than there is any occasion for; only it magnifies the parallax error as well, and the effort to avoid this error strains the eye very unpleasantly. This experience led the writer to the following combination, which he found to give perfect satisfaction. A narrow ivory scale divided into degrees of about 0.1 mm. is fixed slautingly to the needle pretty far down,

yet far enough up for not obscuring the ordinary scale which does duty as usual; on the other hand, a compound microscope of feeble power, which passes through the central fixed portion of the front pane of the case, is fixed slantingly to the pillar. The microscope has one vertical 'wire' in its focus which acts as a needle. As the microscope inverts its images, the apparent motion of the wire in reference to the scale (which one easily persuades himself is fixed) is the same in sense as the real motion of the needle in reference to the ordinary scale, so that mistakes in regard to the + and - are avoided. The ordinary scale is graduated after the micro-scale so that each of its degrees is equal in angular value to  $10^\circ$  of the latter. The writer some five years ago caused Mr. Oertling to apply this arrangement to two of his balances, and he has found it to work very satisfactorily. Although it was originally intended chiefly for special occasions—the adjusting of weights, &c.—it is used even for our everyday work, as it was found that the microscope puts a less strain on the eye than the naked-eye reading of the ordinary scale. The microscopic arrangement described adds about 3*l.* to the cost of the balance. A cheaper arrangement is the following. A micro-scale, divided conveniently into fifth-millimetres, is fixed slantingly to the pillar, the needle at the corresponding

part is shaped thus,  and a hair by means

of capillary perforations is stretched out between *a* and *b*; the hair is parallel to the face of the scale, and only some 0.2 to 0.5 mm. removed from it. A short terrestrial telescope, fixed in the central (fixed) part of the front-pane of the case, serves for the readings. The object glass serves only to produce an image of the scale and hair within the tube, which the eye-piece (a compound microscope) magnifies as far as necessary. As the telescope need not be perfectly steady, it can be fixed at a relatively low cost. We have used this arrangement in connection with one of our balances for over two years, and found it to be almost as good as the one first described.

#### ON THE SETTING UP AND TESTING OF A PRECISION BALANCE.

A real precision balance, to be able to do justice to itself, must stand on a very steady support, in a room where it is not exposed to one-sided changes of temperature. The light should fall in from the back of the observer. The best support, of course, is a pillar of masonry, standing directly on the earth. Next after it (in a substantially built building) comes a shelf fixed to the wall by strong brackets. A good heavy table, however, suffices in practice. In a large city the street traffic becomes very inconvenient in weighing. Its effect can be minimised by putting small pieces of thick vulcanised-rubber plate between the legs of the case and the table. In the examination of a newly set-up balance we naturally begin by seeing that the arrestment, the rider-shifting apparatus, &c. are in good order, we then level the case, and next leave the balance to itself

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for some four hours at least, to enable it to acquire the temperature of the room. After these preliminaries we proceed to the following determinations.

*Determination of the inherent error  $\epsilon$ .*—For this purpose we charge the balance equally on both sides with the highest weight which it is intended to measure (a hectogram-balance for instance with a hundred-gram piece on each side), and after having established approximate equilibrium at the highest degree of sensibility which the balance will stand at this charge without giving obviously inconstant readings, determine the exact position of rest, first with the two hectograms in the centres of their pans, and then, in a series of successive experiments, with one or the other of the hectograms placed at some point of the edge of its pan so as to give any non-parallelism in the axes or any other defect in the terminal pivots a good chance of influencing the result, taking care to interpolate occasionally an experiment with the two weights centrally placed in order to see if the balance still gives the same reading as it did at first. If it does not, this is probably owing to external causes, such as unequal heating of the two arms. To be able to translate degrees of deviation into differences of weight, we must at some stage make two successive determinations of the position of rest, one with *P'* in the left and *P''* in the right pan (*P'* and *P''* stand for the two hectogram-pieces) and another with, say, one milligram added to *P''*. For the precise determination of a position of rest, we cause the balance to vibrate moderately, and (neglecting the first reading as being in general liable to irregularities), record 3, 5, 7 . . . successive turning-points of the needle, applying a + to scale-points lying to the left, and a - to scale-points lying to the right of the zero (or *vice versa*); an odd number in any case in order to correct for the retarding effect of the resistance of the air, &c.; those influences in other words through which the needle, supposing it to start from  $-4^\circ$ , at the end of a double vibration, does not come back to exactly  $-4^\circ$ , but perhaps to  $-3.7^\circ$ . The algebraic sum of any two successive readings gives the point *a* of the scale at which the needle would come to rest, in half-degrees, and there is no reason why the half-degree should not be adopted as a convenient unit for the purpose in hand. Supposing the readings to be

(Example)  $+3.7 \quad -2.7 \quad +3.5 \quad -2.4 \quad +3.5$

we have for *a* the values:  $a_1 + a_2 = +1.0$ ;  $a_2 + a_3 = +0.8$ ;  $a_3 + a_4 = +1.1$ ;  $a_4 + a_5 = +1.1$ . — Mean =  $+1.0$ .

The mean value of the four results is put down as the value of *a*. Supposing *a*, through the addition of  $\Delta$  milligrams to the right charge to increase by *n* demi-degrees, then

$$E = \frac{n}{\Delta} (= 2 \text{ 'E' in the sense of our equation (2)})$$
 is the sensibility in demi-degrees; and its reciprocal  $E^{-1} = \frac{\Delta}{n} \left( = \frac{1}{2E} \dots \text{of equation (2)} \right)$

the weight-value of the demi-degree in milligrams. Supposing the values for *a* obtained with abnormal positions of the charges to be

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$a_1, a_2, a_3$ , &c. instead of the mean value  $a_0$ , corresponding to the centrally placed charges, then  $(a_1 - a_0)E^{-1} = v_1$ ,  $(a_2 - a_0)E^{-1} = v_2$ , &c., give each a value for the *inconstancy* of the balance in milligrams (or rather fractions of a milligram, it is to be hoped). According to a rule deduced from the law of frequency of error, the computation

$$r = \frac{0.845}{\sqrt{n(n-1)}} (v_1 + v_2 + v_3 + \dots)$$

where all the  $v$ 's must be taken as positive, gives the 'probable' weight-value of the deviation of any one  $a$  from  $a_0$ , meaning that value of  $(a_0 - a)E^{-1}$  which, in a *very large number* of determinations, is as often exceeded as not reached. But in practice the number of determinations made is never sufficiently great to bring out anything like a close approximation to the law, and it suffices to take  $r$  as being equal to 0.845 times the mean of all the values  $v$ , and adopt it as sufficiently near to the theoretical ' $\epsilon$ .' The probability that, in a given case,  $(a_0 - a)E^{-1}$  exceeds

$$\begin{array}{cccc} 2r & 3r & 4r & 5r \\ \text{is } 0.18 & 0.04 & 0.007 & 0.0007 \end{array}$$

respectively.

In these determinations, if the balance lacks a microscopic reading arrangement, it is as well to read from a distance with a telescope, to avoid the parallax error which we have no right to charge against the balance.

*Determination of  $h$ .*—All that is necessary is to determine the weight value of one degree in the sense of equation (2) for, say,  $p=100, 75, 50, 25, 0$  grams, and to calculate the corresponding values  $h$ . In a good balance  $h$  is so small that (supposing our rule regarding the adjustment of the bob to be followed), the sensibility remains almost constant from  $p=0$  to  $p=100$  grams. Hence, practically, it suffices to adjust the bob so that at a convenient average charge (where 'average' refers to the most frequently occurring values of  $p$ ) one demi-degree corresponds to say  $\frac{1}{2}$  or  $\frac{1}{3}$  of a milligram *exactly*, and then to see what it is at other charges. If there is no sufficient constancy we enter the values  $E^{-1}$  found on a system of rectangular co-ordinates in function of the charges  $p$ , and draw the nearest curve to the points. This curve (if  $h$  were absolutely constant) would be a straight line. In any case it supplies the data for a table of values for  $E^{-1}$ . This table, however, must not be relied on in *standard* weighings, because the value  $h$  is subject to changes, for this reason amongst others, that the agate of the knives has a different co-efficient of expansion from the metal of the beam.

*The arm-lengths.*—For the determination of the ratio of the arm-lengths, the orthodox method (for a hectogram balance) is to adjust two hectogram-pieces to exact equality, and, after having established equilibrium, to put one into the left and the other into the right pan, &c. But in practice the following method is better. Take any two fairly well adjusted hectograms, and viewing them, one as a *standard* representing 100,000, the other as an *object* weighing  $x$  milligrams, go through the ordinary operation of weighing once with the object in the left pan

and the standard in the right, and once the other way.

Supposing (using  $S$  as a symbol for 100,000 milligrams) we find

$$\begin{array}{llll} xI' = (S + \delta_1)l' & : & : & : & I \\ xII' = (S + \delta_2)l' & : & : & : & II \end{array}$$

(where any  $\delta$  may be negative) we have by division of I by II, and subsequent multiplication with  $l'' : l'$ ,

$$\left(\frac{l''}{l'}\right)^2 = \frac{S + \delta'}{S + \delta_2} = \frac{1 + \frac{\delta_1}{S}}{1 + \frac{\delta_2}{S}}$$

whence, as a sufficient approximation,

$$\frac{l''}{l'} = 1 + \frac{1}{2} \left( \frac{\delta_1 - \delta_2}{S} \right).$$

No maker who has a name to lose would care to send out a precision balance in which

$1 - \frac{l''}{l'}$  is more than  $\pm 0.00005$  at the outside, al-

though for any scientific purpose a considerably greater error could be tolerated. The corresponding adjustment indeed, while of the first importance in commercial balances, in precision balances is in a sense irrelevant.

#### UNEQUAL-ARMED LEVER BALANCES.

(1) *The steelyard or Roman balance.*—In it only the shorter arm (of the length  $l$ ) bears a pan; the longer arm, by notches cut into its back, is divided into parts of equal length,  $l$  being the unit. The working points or lines of the notches should lie in the plane of the two edges, being so many bearings for the knife-edge forming part of a sliding weight adjusted to  $P$  units. The unloaded balance is in its position of rest when the beam stands horizontal. To weigh a body, it is placed in the pan and the sliding weight shifted forwards from notch to notch until (when the weight hangs at the distance  $nl$  from the axis of rotation) the beam is again at rest in its horizontal position. We then have for the weight sought

$$x l = n l P \text{ or } x = n P.$$

As fully explained above, the principle of the steelyard is discounted in the modern precision balance for the determination of small differences of weight. In theory there is no objection to its extension to the determination of weights generally, but the technical difficulties to be overcome are great. On an equal-armed balance, whose beam is divided into 100 equal parts (from end to end), all weights from 0.0001 to 100 grams might be determined with three riders weighing half of (100, 1, and 0.01) gram respectively, but the realisation of 101 exact pivots is no small matter. Where relatively high precision is aimed at, it is better to provide only a small number of notches (say 10) and have a set of riders, weighing say 10, 1, 0.1, 0.01 grams respectively. The specific gravity balances of Westphal of Celle, are made on this principle. It strikes us that the steelyard principle might be discounted for the decimal subdivision of weights, thus:

Imagine a precision balance whose two arms measure 10  $l$  and 11  $l$  units. 10 grams placed in the pan of the longer arm are balanced by 10 + 1 grams placed in that of the shorter; hence a

1 gram piece may be adjusted after two exact 10 gram pieces, &c.

The *tangent balance* has only one short arm, from which the pan is suspended; its centre of gravity lies low, so that the *momentum stativum*  $Ws$  of the beam assumes a high value, and even a considerable weight placed in the pan produces only a moderate angle of deviation. The needle moves along a circular limb divided so that the readings are proportional to the tangents of the respective angles of deviation, and give the corresponding weights directly. The equation

$$\Delta = \frac{tga \cdot Ws}{l} \quad (\text{see equation (1) above}) \quad \text{holds theo-}$$

retically for any value  $\Delta$ , but the angular deviation corresponding to 1 gram of additional charge becomes less and less as the charge increases. The tangent balance, though useful for the rough weighing of letters, parcels, &c., is not available for exact gravimetric work.

#### COMPOUND LEVER BALANCES.

In all these, practical convenience and rapid working are gained at the expense of precision. In the *Roberval balance* the pans are above the system of levers (which as a rule is concealed in a box), so that there is room for bodies of even large dimensions. Our diagram, fig. 8, is intended to explain only the *principle* of the machine, which in practice assumes an endless variety of forms.

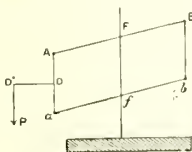


FIG. 8.

The beam consists of two parallel vertical parallelograms of which only the front one is represented in our figure.  $F$  and  $f$  (and  $F'$  and  $f'$  in the other parallelogram) are fixed pivots,  $A, B, a$  and  $b$  ( $A', B', a', b'$  behind) are movable joints. On each side a horizontal bridge connects a point  $D$  on the vertical side  $Aa$  (and a similar point on  $Bb$ ) with a corresponding point  $D'$  on the back parallelogram (so that for instance,  $Aa, A'a', D, D'$  form one piece) and, from the centres of these bridges, vertical rods are rising which support the pans. Supposing each pan to be charged with  $P$  pounds, the centre of gravity of either of these two equal charges may lie in any of a great many positions about the respective pan, yet the statical effect is the same as if it were concentrated, one in the centre of the one bridge, and the other in the centre of the other; the two charges will balance each other, because, if the centre of gravity of one descends by  $h$  mm. that of the other rises by  $h$  mm., so that the work  $P h$  is the same on both sides. An over-weight added to one of the charges will bring down that side. The bars  $AB$  and  $A'B'$  are relatively heavy beams, the lower bars  $ab$  and  $a'b'$  are light. Hence it depends chiefly on the distribution of the mass in the beams  $AB$  and  $A'B'$  whether the balance (if nearly equally charged) has a definite position of rest; but even if it has, it will never

vibrate like an ordinary balance, on account of the great friction in the numerous pivots. If it could only be cured of this defect, the Roberval would be the ideal balance for the counter or ordinary weighings in the laboratory. This problem has been to some extent solved in the torsion balance of Springer, in which the axes are realised in stretched out horizontal bands of elastic steel, which act, so to say, as knives and bearings in one.

The '*torsion balance*' is made<sup>1</sup> in a great variety of forms, but the principle of construction is the same in all. The following description is

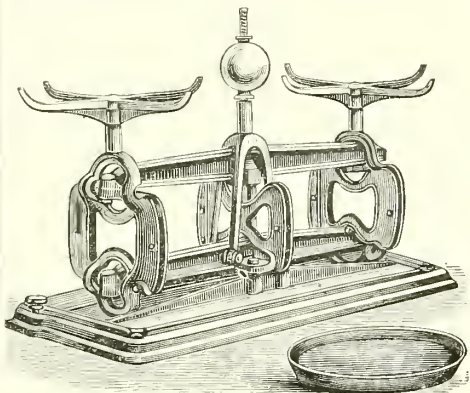


FIG. 9.

based upon the examination of what was sold as a high-class pair of counter-scales for loads up to 20 lbs. As shown by fig. 9, the balance consists of two parallel beams united into a flexible

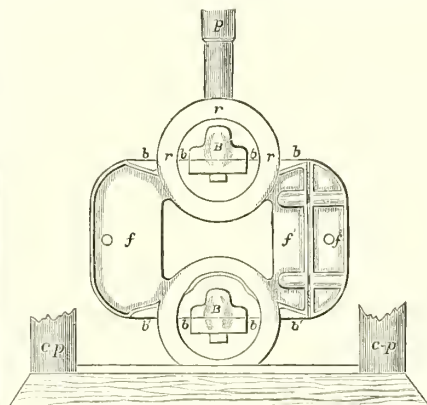


FIG. 10.

parallelogram by means of three vertical frames, the bond of union in the case of each frame consisting of two horizontal bands of elastic steel, which bridge over certain gaps of the frames, the middle portion of each band being firmly united with the respective beam end at its lower side by means of a screwed-on block of metal. In this instrument the beams measure 290 mm.

<sup>1</sup> By the Torsion Balance and Scale Company, 92 Reade Street, New York.





least a fixed function of  $P$ ; hence the path of  $a$  can be graduated, at least empirically, so that each point of the scale corresponds to a fixed number of units of weight. This is the general principle of the multitude of *spring balances*. Sometimes a relatively strong spring is used to effect only a small displacement of  $a$  even with the highest charge, but this displacement is then multiplied by a system of levers, so that the least difference of weight which the balance is meant to show becomes visible. In a very neat kind of spring-balance, which has become popular, the displacement of  $a$  is, by means of levers and a toothed wheel, translated into the circular motion of a needle which moves along a divided circular limb like the hands of a clock on their dial.

Jolly constructed a *quasi* precision spring-balance for sp gr. determinations thus:—A long spiral of wire is suspended vertically in front of a vertical millimetre-scale, etched on a strip of plate glass which is silvered behind, so as to avoid the error of parallax. From the lower end of the spiral a light pan is suspended; the index is close above the pan at a convenient point. The instrument has never come into general use, because any second-class precision balance beats it in every sense. A similar remark, applies to an ingenious little instrument invented by Ritchie for the determination of minute weights.

*Ritchie's balance* consists of a very light beam whose axis of rotation passes through its centre of gravity, and which is firmly united with a thin horizontal wire which lies in the axis of rotation. The hind end of the wire is absolutely fixed to the stand; the front end forms the continuation of the axis of a circular pin revolvable within a circular bearing. A needle fixed radially to the pin points to a divided circular limb. The empty balance is so arranged before use that the beam when horizontal is at rest. To determine a small weight ( $x$  mgr.), it is placed in, say, the right pan, and the wire turned from the right to the left by turning the pin until after the needle has passed through  $\alpha$  degrees (where  $\alpha$  may be more than  $360^\circ$ ); the beam is again at rest when horizontal. We then have  $x = \text{const. } \alpha$ . The constant must be determined by experiments with known weights. Sartorius of Göttingen used to apply the Ritchie arrangement to his precision balances for the determination of differences of weight from 10 mgrs. downwards (Bibl. 5), but he has long since given up the notion: at any rate it is no longer to be seen in his price-list. A Ritchie balance might perhaps do well for the adjusting of small weights, but a small precision steelyard would work infinitely better.

Sartorius' combination, if provided with a relatively strong wire, might make a handy instrument for the rapid (approximate) determination of weights without the use of any standard mass less than one gram.

#### THE HYDROSTATIC BALANCE

is a hydrometer provided with a relatively large body and a narrow neck, and so adjusted that it weighs considerably less than its own volume of water. The top end of the neck bears a horizontal table, which serves as a pan, or, what is

better, is provided with a horizontal system of cross-bars, from whose ends a pan is suspended by means of wires or chains, below the shelf supporting the vessel containing the floating hydrometer. A certain weight  $P$ , placed in the pan, brings down the hydrometer so far that the surface of the water touches a certain mark on the stem. If an unknown weight  $x$  requires to be supplemented by standard weights equal to  $p$  units, to produce the same effect,  $x + p = P$ , or  $x = P - p$ . Even for  $P =$  let us say 2 kilos., the neck need not be thicker than an ordinary knitting needle, so that the milligram, as a difference of weight, becomes perceptible. Whenever a precision balance has to be extemporised this instrument is useful; but it has no other *raison d'être*. Indeed of all the multitude of machines which the science of mechanics places at our disposal for the measurement of weights, the equal-armed lever-pendulum is the only one which, so far, has worked satisfactorily for precise gravimetric determinations.

A balance based on dynamical principles has been proposed. Imagine a pendulum provided with a shiftable bob above the fulcrum, and carrying a pan attached to the bottom end of the rod by a hook-and-eye. In a given instrument the time of vibration is a function of the distance of the bob from the fulcrum, and of the weight  $x$  of the object in the pan, and consequently the weight  $x$  is a function of the other variables.

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(3) *Löwenherz*; Report on Metrological Instruments in Bericht über die wissenschaftlichen Apparate auf der Londoner Ausstellung in 1876; Braunschweig, 1881. Vacuum Balances, 223-232. Balance Beams, 232-237. The Pivots: Modes of Fixing the Knives, 237-245; Bearings, 246-247; Arrestments, 248-253.

(4) *Löwenherz*; Zeitschrift für Instrumentenkunde for 1881, 125; Report on Sartorius' Hinged Arrestment Frame.

(5) *Löwenherz*; same Journal, year 1881, 184. A Report on Apparatus for Measuring Small Weights by the Torsion of Wires: Hooke, Ritchie, Sartorius. Full drawing of Sartorius' contrivance on page 188.

(6) *Dittmar*; Waage des Chemikers; same Journal, year 1881, 313-326.

(7) *Dittmar*; same Journal, year 1882, 63; Mikroskopische Ablesungsvorrichtung für feine Waagen.

(8) *Dittmar*; R. Soc. Ed., Proc. for 1876; C. N. 33, 157. W. D.

#### BALANOPHONE WAX v. WAX.

**BALATA.** The guta of two species or subspecies of the bully- or bullet-tree, *Mimusops Balata* and *M. globosa* (order Sapotaceae), found in Jamaica, Trinidad, Venezuela, British and French Guiana. The sap of the bullet-tree is extracted from the laticiferous cells of the bark by means of incisions made in the tree, either as it stands or after being felled. In the former case the life of the tree may be spared by careful tapping,

or sacrificed by ignorant or careless treatment. As the milk drops from the wounds thus made it is collected in calabashes, which are emptied from time to time into larger vessels, in which the produce is carried to the encampment where the drying takes place. The product of a growing tree of 16 to 20 inches diameter, bled upward from its base to 8 feet high—i.e. as far as a man standing on the ground can reach with his axe—is about 3 pints of milk; if a ladder is used the yield may be twice as much. An active man will thus collect from 2 to 5 gallons of milk in a day, going from tree to tree. The quantity extracted from a felled tree is several times greater, an average good size tree yielding 4 gallons of balata milk, equal to 20 pounds of the dried substance.

The milk is remarkably white, which appearance it will retain for a long time if sealed up after the first slight fermentation which follows its collection has taken place. In drying by exposure to the air it becomes externally a dark brown, but when precipitated by spirit it remains white. The loss by drying of an average sample of milk is less than one half of its weight. A sample gathered in British Guiana in the month of April, when the rain was light and the sap consequently in a normal condition, contained, water 39.04 p.c., balata 60.31 p.c., and mineral matter 0.65 p.c.

According to Hugo Müller balata combines the characteristics of gutta-percha and india-rubber. Its strength is very great, and it does not stretch under tension. Its electrical insulating property is quite equal to that of gutta-percha.

According to Bolas, balata is simply an excellent quality of gutta-percha. Its chemical composition is identical with that of gutta-percha and caoutchouc.

**BALDWIN'S PHOSPHORUS** *v.* **CALCIUM.**

**BALL SODA** *v.* **SODA MANUFACTURE.**

**BALLOON** *v.* **FLEXIBLE VARNISH** *v.* **VARNISH.**

**BALM OF COPAIBA** *v.* **OLEO-RESINS.**

**BALM OF GILEAD**, *Mecca- or Opobalsam*, *v.* **OLEO-RESINS.**

**BALSAMS.** The exudations of plants, whether spontaneous or promoted by incisions made in their stems or roots, consist chiefly of resin, gum, volatile oil, and certain aromatic acids, or mixtures of these. The *resins* are characterised by insolubility in water and solubility in alcohol, the *gums* by solubility in water and insolubility in alcohol, and both by not being volatile without decomposition. *Volatile oils* may be distilled unchanged, and are solvents of resins. They are not obtained by the method of exudation except when they hold large quantities of resin in solution, giving rise to the important class of *oleo-resins*—such, for instance, as the so-called Canada balsam. Gum arabic is a familiar instance of a gum obtained direct from the plant; mastic is an instance of a resin. The class of *gum-resins* may be represented by myrrh.

Now amongst these resins and oleo-resins there is a group the members of which are marked by possessing a peculiar fragrant odour and agreeable pungent taste, which is due to the presence of free or combined cinnamic or ben-

zoic acid. These are the *balsams*, and it is convenient to consider them as a class by themselves. The word balsam, it is true, has sometimes been used in a wider sense, indeed it was originally employed for an oleo-resin resembling the so-called Canada balsam; but it is more convenient to restrict the term to resins or oleo-resins which contain cinnamic or benzoic acid. The balsams have long been familiar to writers on materia medica, some of them being known to Pliny, and even earlier to the Greek physicians. They are favourite constituents of the incense used in the Greek and Roman churches, and while they cannot be said to have an important therapeutic value, they are reputed mild tonics and stimulants and are a common flavouring agent in expectorant medicines. The following are the more important:—

**Benzoïn.** *Gum Benjamin; Benzoinum; Benzoin* (Fr.); *Benzoinharz* (Ger.). The benzoïn of Java and Sumatra is derived from the thick-stemmed trees of *Styrax Benzoin* (Dryander, Tr. 1787, 303; Benth. a. T. 169), while the more highly prized Siam benzoïn is probably obtained, according to Royle, from the *Styrax Finlaysonian* (Wall). The source of Siam benzoïn is, however, still uncertain (Holmes, Ph. [3] 14, 354). The first European writer to mention benzoïn is Batuta, who travelled in the East early in the fourteenth century, and from that time to the present day the drug has been an established article of materia medica. It is largely used for incense and in the preparation of fumigating pastilles, and enters into the well-known Friar's Balsam or compound tincture of benzoïn, a favourite dressing for wounds.

The juice exudes from the trees as the result of incisions, and it is allowed to harden before it is removed. During the first three years of the life of a tree the balsam dries in the form of *tears*. This is called *head benzoïn* and is the most highly reputed. A less esteemed variety is obtained during the following seven or eight years, which is browner in colour and is called *belly benzoïn*. Lastly, the trees are split, and the commoner *foot benzoïn* is scraped off (*cf.* Fl. a. H. 405).

Benzoïn consists essentially of a mixture of resins together with uncombined benzoic and sometimes cinnamic acids. The resins are entirely soluble in solution of potash and in alcohol, but by their behaviour toward other solvents they have been distinguished as *α-resin*, *β-resin*, &c. (Unverdorben, P. 8, 337; Kopp, C. R. 19, 1269; Van der Vliet, A. 34, 177). The yield of *benzoic acid* varies from 12 to 20 p.c., being on an average about 14 p.c. Two methods are adopted for its extraction. By the first the benzoïn is mixed with sand and heated in a suitable vessel, over which is placed a paper or other receiver to collect the vapours of benzoic acid, which condense in beautiful tufts of acicular crystals. The second method consists of boiling the benzoïn with milk of lime, filtering, and after concentration of the calcium benzoate solution thus obtained, precipitating the benzoic acid by hydrochloric acid. *Cinnamic acid* was detected in Siam and Pénang benzoïn by Kolbe and Lautemann (A. 115, 113; 119, 136); and in Sumatra benzoïn by Aschhoff

(J. 1861, 400). Beuzoïn contains traces of volatile oil. Rump (B. 11, 1634) found *vanillin* in Siam benzoïn. Siamese benzoïn has been further examined by Hirschsohn (P. Z. 23, 601). Compare also Wiesner (J. 1872, 1060), Deville (A. Ch. (3) 3, 192), Theegarten (J. 1874, 922), and Ciamician (B. 11, 274).

Benzoïn, with the exception of woody fragments always present in the cake variety, should dissolve in five times its weight of alcohol, and this solution should give with water a milky emulsion having an acid reaction. When benzoïn is boiled with milk of lime, the hot filtrate should not give off the odour of oil of bitter almond on the addition of a solution of permanganate of potassium. This latter test guards against the addition of cinnamic acid (cf. U.S. and Ger. Pharm.).

**Peru.** *Balsamum Peruvianum*; *Banme de Pérou* (Fr.); *Perubalsam* (Ger.).

A dark molasses-like liquid obtained in the State of Salvador in Central America from trees of *Myroxylon Pereira* (Klotzsch). Description v. Benth. a. T. 83. Balsam of Peru was probably introduced into Europe soon after the Spanish conquest of Guatemala in 1524 (Fl. a. H. 206). The bark is bruised and scorched late in the autumn, and the exudation excited by this means is collected (Fl. a. H. 207; Dorat, Am. J. Pharm. [3] 8, 302; Hanbury, Ph. [3] 5, 241, 315).

Balsam of Peru sinks in water, in which it is insoluble. It has a sp.gr. of 1.135 to 1.150. It is soluble in absolute alcohol, chloroform, acetone, and glacial acetic acid. Examined by Kraut (A. 152, 129) and Kachler (B. 2, 512), the chief constituent of Peru balsam was found to be *cinnamēn* or benzyl cinnamate  $C_6H_5 \cdot CH : CH \cdot COOC_6H_5$ . As obtained from balsam of Peru, this ether has not yet been crystallised, but in other respects it agrees with that produced by the action of benzyl chloride on an alkaline cinnamate. Kachler's analysis of Peru balsam is:—Cinnamic acid 46 p.c., benzyl alcohol 20 p.c., resin 32 p.c. Cf. Attfield (J. 1863, 557); Delafontaine (Z. 1869, 156) finds, in addition to benzyl cinnamate, *cinnamyl cinnamate* or *styracin*  $C_6H_5 \cdot CH : CH \cdot COOC_6H_5$ . This observation is confirmed by the recent investigation of MacEwan (Ph. [3] 15, 236). Treating the balsam with petroleum ether (b.p. 65°). MacEwan finds that the cinnamēn, together with a little free cinnamic acid, dissolves. The proportion obtained in good specimens ranges from 4 to 50 p.c. The residue, treated with carbon bisulphide, gave to that solvent on an average about 35 p.c. of an oil with an odour of storax. This oil, subjected to the action of alcoholic potash, gave oily drops of what appeared to be cinnamyl alcohol, and thus, in view of Delafontaine's previous observations, there cannot be much doubt that the balsam contains about a third of its weight of styracin. The residue left by the bisulphide consisted of *resin*, which, according to MacEwan and Schlickum (Ar. Ph. [3] 20, 498), is not present to a greater extent than 16 p.c., though previous writers have stated it as high as 40 p.c. Melted with potash the resin yields protocatechuic acid and benzoic acid (Kachler).

Balsam of Peru has been much adulterated. Alcohol, fixed oils, copaiba, Canada turpentine,

colophony, &c., have been used for this purpose. To ascertain its purity many methods have been devised. The specific gravity is important; this at once indicates alcohol if present. Alcohol may also be washed out by water and the reduction in volume noted. The U. S. Pharm. directs 10 drops of the balsam to be triturated with 20 drops of sulphuric acid, when a tough homogeneous cherry-red mixture should result. If this be washed after a few minutes with cold water it should be converted into a resinous mass, which is brittle when cold. This test indicates the absence of fixed oils and oleo-resins. For other modes of testing v. Hirschsohn (P. Z. 16, 81); Flückiger (Ph. [3] 12, 45); Schlickum (Ar. Ph. [3] 20, 498); MacEwan (Ph. [3] 15, 236); Andrée (Ar. Ph. [3] 22, 561). Testing of balsams, resins, and gum-resins (Ph. [3] 17, 547).

A *White Peru Balsam* is sometimes prepared in Salvador by expression from the fruit of the *Myroxylon Pereira*. It is a golden yellow semi-fluid granular crystalline mass containing a crystalline resin, *myroxocarpin*  $C_{21}H_{31}O_3$ , together with *styracene*, *styracin* and *cinnamic acid* (Stenhouse, A. 77, 306; Pereira, A. 77, 309; Scharling, A. 97, 70; Harrison a. Malsch, J. 1875, 856). For other varieties of Peru balsam, v. Fl. a. H., 210.

**Storax.** *Liquid Storax*; *Balsamum Styracis*; *Styrax Liquide* (Fr.); *Flüssiger Storax* (Ger.).

Storax balsam is derived from trees of *Liquidambar orientalis* (Miller), which are natives of Asia Minor (cf. Benth. a. T. 107). This liquid storax is nearly related to another harder resin—the exudation of the *Styrax officinalis* (Linn.). Both have been known since the later Greek period, but the latter is now no longer an article of commerce. To obtain the storax the outer bark of the tree is removed and rejected, and the inner bark is collected and boiled in water. The balsam melts and is carried to the surface and skimmed off.

Liquid storax is heavier than water, about the consistence of honey, and of a greyish-brown colour. It always contains a little water, which imparts to it a greyish opacity. When this is removed, by long standing or by heat, the resin becomes quite transparent. Dried in this way it is soluble in alcohol, ether, carbon bisulphide, and volatile oils; but not in petroleum ether. The odour of storax is agreeably balsamic and the taste aromatic and pungent. Examined with a microscope crystals may be detected which have been identified, the feathery spicular crystals as styracin, and the rectangular tables and short prisms as cinnamic acid.

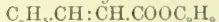
Storax contains 10 p.c. to 20 p.c. of water, 13 p.c. to 18 p.c. of woody and inorganic impurities, leaving 56 p.c. to 72 p.c. of matter soluble in alcohol, which consists chiefly of styracene, metastyracene, cinnamic acid, styracin, and a large proportion of resin (Fl. a. H., 275).

*Styracene* or phenylethylene  $C_6H_5 \cdot CH : CH_2$  is obtained as a colourless mobile liquid by distilling storax with water (Bonastre, J. Pharm. 16, 88; Simon, A. 31, 267). The solid polymer of styracene, *metastyracene*, is also said to exist in storax. *Cinnamic acid* to the extent of 6 p.c. to 12 p.c. is obtained by boiling the balsam with alkaline carbonate solution, which extracts it as



a sodium salt from which the free acid is liberated by mineral acids.

*Styracin or cinnamyl cinnamate*



was originally discovered in storax by Bonastre. It may be obtained, after removal of the styrolene and cinnamic acid by treatment of the residue with ether, alcohol, or petroleum ether, in the form of a liquid, which with difficulty assumes a solid crystalline form, the crystals melting at  $44^\circ$  (Simon, A. 31, 273; Toel, A. 70, 1; Miller, A. 188, 200). Styracin is readily converted by alkali into styrone or cinnamyl alcohol and cinnamate. *Benzyl alcohol* has been detected as a constituent of storax by Laubenhimer (A. 164, 289). A good bibliography will be found in W. von Miller's memoir on the Chemical Compounds contained in Liquid Storax (A. 188, 184), in which the author describes as present, in addition to the constituents already mentioned, *phenylpropyl cinnamate*, *ethyl cinnamate*, *ethyl vanillin*, large quantities of two alcoholic compounds,  $\alpha$ - and  $\beta$ -*storesin*, and their cinnamic ethers, a sodium compound of *storesin*, and a *resin*.

Storax is sometimes adulterated with turpentine. To detect this Hager dissolves the balsam in a little warm alcohol, and shakes this solution with petroleum ether. The petroleum ether on evaporation leaves a residue in which the terebinthinous odour is concentrated, and may be readily detected. Further, the residue so obtained, in the case of genuine storax, is colourless with a bluish opalescence, and represents 45–55 p.c. of the original balsam; but if turpentine be present the percentage is larger, and the residue has a yellowish colour (Ph. Centh. 15, 163).

Closely allied to liquid storax are the exudations from the *Styrax officinalis* (Linn.); *Liquidambar styraciflua* (Linn.), a native of North America, the balsam of which has been recently examined by Flückiger and v. Miller (Ar. Ph. (3) 20, 646 a. 648); *Liquidambar formosana* (Hance); and *Altingia excelsa* (Noronha) (cf. Fl. a. H., 276).

*Tolu*. *Balsamum Tolutanum*; *Baume de Tolu* (Fr.); *Tolubalsam* (Ger.).

Monardes, in his book published in 1574 describing the products of the West Indies, is the first to mention balsam of tolu. Soon afterwards it was introduced into England. Tolu is the product of the trees of *Myroxylon Toluifera* (H. B. a. K.), natives of Venezuela and New Granada, and probably also of Ecuador and Brazil. For botanical characters, v. Benth. a. T. 84. V-shaped incisions are made, and the concreted juice from time to time collected. This draining of the trees goes on for eight months of the year (Weir, Journ. R. Hort. Soc., May, 1864).

Balsam of tolu is a viscid resin, which on exposure hardens to a vitreous consistence. It has an agreeable odour suggestive of vanilla, and has a decided aromatic taste. Crystals of cinnamic acid may be seen in tolu when thin layers are examined. It is soluble in alcohol, glacial acetic acid, acetone and chloroform, also in caustic potash. In benzene it is insoluble, and nearly so in carbon bisulphide, volatile oils, and ether. Balsam of tolu consists for the most part of an *amorphous resin* similar to that left by carbon bisulphide in the case of Pern balsam. This

was shown by Kopp (J. 1847–8, 736) to consist of two resins, distinguished by their different solubilities in alcohol and a difference in their melting points (cf. Scharling, A. 97, 71). Treatment with water extracts from balsam of tolu *cinnamic acid* (Carles, J. Ph. 19, 112), and according to Lasse (B. 9, 830) it contains also *benzoic acid*, and both *benzyl benzoate* and *cinnamate*. Distilled with water, small quantities of a peculiar hydrocarbon pass over which has been called *tolene*. The yield, according to Deville, is 2 p.c. (A. Ch. [3] 3, 152). Toluene has the formula  $\text{C}_{10}\text{H}_{16}$ . Its specific gravity at  $10^\circ$  is '858 (Kopp), and it boils at  $170^\circ$ , according to Deville and Scharling, or at  $154^\circ$ – $160^\circ$  (Kopp). Deville found toluene to have a vapour density of 5.1. This hydrocarbon does not appear to have been further studied or to be known in any other chemical relation.

Turpentine present as an adulteration in tolu may be detected by treatment with carbon bisulphide, which has scarcely any solvent action on the genuine balsam; or by sulphuric acid, which imparts to tolu a cherry-red colour, whereas when turpentine is present the mixture turns black. A specimen of spurious tolu examined by Naylor was completely soluble in carbon bisulphide (Ph. [3] 8, 624).

**Xanthorrhœa Balsams.** A number of balsamic resins are obtained from the xanthorrhœas or grass trees of Australia. Seven species of these, the *arborea*, *australis*, *Hastile*, *media*, *minor*, *bracteata*, and *Pumilio* were described as early as 1810 by Brown (Prodromus Novæ Hollandiæ). The first two are arborecent trees, the third and fourth have short stems, and the last three are stemless. Hirschsohn (Ph. Z. 16, 81) distinguishes three xanthorrhœa balsamic exudates; but of these only two are important, the *yellow* or *acaroid balsam* and the *red balsam* (Pereira, Mat. Med. 3rd edit. 1099).

**Acaroid Balsam, Acaroid Resin, Resina Acaroides, Resin of Botany Bay.** This balsam was first mentioned by Governor Phillips in 1789 (Voyage to Botany Bay). It exudes spontaneously from the *Xanthorrhœa Hastile* and, according to some writers, from the *X. arborea*. It has a yellow colour resembling gamboge, but sometimes has a deep red tint, and when heated evolves a balsamic odour. It is used in the preparation of sealing-wax and lacquers and janniper's gold-size. Amongst those who have investigated acaroid balsam are Liechsteuine (Crells Ann. 2, 242); Schrader (Trommsdorff's Ann. 5, 96); Laugier (A. Ch. 76, 265); Widmann (Buchner's Report. 22, 198); and Stenhouse (C. S. Mem. 3, 10; A. 57, 84). Its chief constituents are *resin*, a trace of *volatile oil*, and both *cinnamic* and *benzoic acids*. These latter are precipitated from a solution of the balsam in caustic potash by the addition of hydrochloric acid. By distilling it alone Stenhouse obtained a light neutral oil containing *benzene* and *cinnamene*, and by treatment with nitric acid the same observer finds acaroid balsam to give so large a yield of *picric acid* that he recommends it as a convenient source of that compound. As much as 13 p.c. of *parahydroxybenzoic acid* is formed when acaroid balsam is fused with potash. Amongst the other products of this reaction, are *resorcinol*, *pyrocatechol*, and

a double compound of parahydroxybenzoic and protocatechuic acids  $C_{11}H_{12}O_2 \cdot 2H_2O$ , which has been likewise obtained from benzoïn (Illasiwetz and Barth, J. 1866, 630).

*Red Balsam of Xanthorrhæa.* *Black-boy Gum.* A red balsamic resin resembling dragon's blood. When heated it evolves a balsamic odour. Compare Maisch on Xanthorrhæa Resins (Am. J. Pharm. [4] 11, 217). A. S.

**BAMBARA BUTTER** v. **BASSIA OILS.**

**BAMBOO.** The ash of the shoots of this grass (*Bambusa arundinacea*, *verticillata*, &c.), contains of potash ( $K_2O$ ) from 30 to 40 p.c. The Forest Department of Burmah are therefore cultivating the bamboo as a source of potash. The fibres of the shoots supply an excellent paper-making material (Romanis, C. N. 45, 158; 46, 51; N. 18, 50).

**BAMBUI BUTTER** v. **BASSIA OILS.**

**BARBERRY ROOT.** The root of *Berberis vulgaris*, a wild shrub common to Europe and Asia. The active principle which it contains is the alkaloid *berberine*  $C_{20}H_{17}NO_4 \cdot 5H_2O$ , which may be prepared by boiling the root with water containing a slight excess of lead acetate, filtering, and evaporating the filtrate to crystallisation. Berberine crystallises in fine yellow prisms, very soluble in hot water and alcohol, but insoluble in ether. It begins to sublime at  $200^\circ C$ . The salts of berberine are sparingly soluble. The hydrochlorate and phosphate are used medicinally.

Berberine is also found in the root, wood, or bark of the following plants: *Berberis aristata*, *Xanthoxylon clava-Herculis*, *Hydrastis canadensis*, *Coscinium fenestratum*, *Jaleorhiza palmata*, *Xylopia polycarpa*, *Podophyllum peltatum*, *Xanthorissa apii folia*, *Coptis lecta*.

The root, root-bark, and especially concentrated liquid extracts of the same, are used to a small extent for dyeing silk and leather yellow. It is the only natural basic colouring matter at present employed. Wool and silk are dyed in a neutral bath, or with a slight addition of alum to the dyebath. It gives somewhat clear yellow shades, not remarkable, however, for any special quality either of fastness or purity of colour.

*Literature.*—Buchner, A. 24, 228. Fleitmann, *idem*, 59, 160. Boedeker, *idem*, 66, 384; 69, 40. Dyson Perrins, *idem*, Suppl. 2, 171, and 83, 276. Stenhouse, *idem*, 95, 108. Repert. chim. appl. 4, 459. Repert. chim. pure, 3, 105; 4, 367; 5, 423. A. 115, 132; 122, 256; Suppl. 1863, 2, 191. Journ. chim. med. 1826, 2, 314. C. J. 15, 339. Bl. 1863, 423; C. J. Abstr. 1885, 675; 1886, 633, 1041; 1887, 174, 383, 505, 1057; C. J. 1889, 63; Ar. Ph. [3] 26, 329; 25, 164; Am. S. [2] 33, 43; A. 24, 228; A. Suppl. 2, 197. J. J. H.

**BARILLA**, or **BARILLOR** (Fr. *Barille*). Commercial name of an impure soda obtained from the ashes of the *Salsola Soda*, which was formerly grown specially in Spain, Sicily, Sardinia, the Canary Islands, and the Levant. The seed was sown at the end of the year, and the plants were ready for cutting in September of the following year; they were usually burnt during October. A hole capable of holding one or two tons of soda was dug in the ground and covered over with an iron grating; the dried plants, mixed with canes, were heaped on this and set

on fire. The heat was sufficient to melt the ash, which ran down and collected in the hole. More material was supplied to the fire till the hole was full of fused soda; it was then covered with earth and left to cool, after which the porous mass was broken out and was ready for shipment. Contained about 20 p.c. alkali, together with chlorides and sulphates of Na, Ca, and Al, and very little S. Formerly much used for making soda soap; little, if at all, used now.

Kelp is sometimes called *Barilla*.

**BARIUM.** Symbol Ba. At. w. 137.

The name 'barote' (from *βαρύς*, heavy) was given to the earth contained in heavy spar (*terra ponderosa*) by Guyton de Morveau in 1779, and was afterwards altered to 'baryta' by Lavoisier; the name itself, therefore, is indicative of the great density of its compounds. Barium occurs principally as the sulphate, *barytes* or *heavy spar*  $BaSO_4$ , and is generally found associated with metallic ores containing sulphur. Dieulafoy (A. Ch. [5] 15, 530) has shown that all primary rocks contain barium in sufficient quantity to be easily detected. Barium also occurs in nature as *witherite*  $BaCO_3$ , *baryto-celestite*  $(BaSrCa)SO_4$ , *baryto-calcite*

$BaCO_3 + CaCO_3$ , *alstonite*  $(BaCa)CO_3$ , and in certain varieties of the ores of manganese; also in certain silicates, as *brewsterite*  $H_2(SrBa)Al_2Si_2O_{18} + 3H_2O$ , *harmotome*  $H_2(K_2Ba)Al_2Si_2O_{13} + 4H_2O$ , and *hyalophane* or *baryta-felspar*  $K_2Ba \cdot 2Al_2Si_2O_{12}$ , and frequently in mineral waters. Barium is also frequently found in calcium and strontium minerals, replacing a portion of those elements with which it is isomorphous.

It is never found native; indeed, according to Donath (B. 12, 745), it is questionable whether pure metallic barium has ever yet been seen except as a metallic powder. Its oxide, baryta  $BaO$ , was first recognised as a peculiar earth distinct from lime by Scheele in 1774, and the metal itself was supposed to have been isolated by Davy in 1808; but Davy's 'metal' has been since shown to consist of an amalgam of barium with as much as 60 p.c. of mercury.

*Preparation.*—1. Davy's method of preparing barium was as follows:—Barium hydrate, chloride, nitrate or carbonate, was made into a thick paste with water, kneaded into the shape of a cup, and placed upon a platinum dish connected with the positive pole of a very powerful voltaic battery, the negative pole of which was connected by means of a wire with a quantity of mercury placed in the cup. The salt of barium was thus electrolysed and an amalgam of barium and mercury formed; this amalgam was then heated in a tube of glass free from lead and filled with the vapour of rock-oil till the mercury ceased to sublime. If oxide of mercury be mixed with the barium hydrate the yield of barium, according to Davy, is considerably increased. Hare (J. pr. 19, 249) prepared the amalgam from moistened barium chloride surrounded by a freezing mixture, using 200 cells containing over a hundred square feet of zinc, and expelled the mercury by heating the amalgam in an iron crucible exhausted of air.

2. Impure barium may also be obtained, according to Davy, by passing vapour of potassium over red-hot baryta or barium chloride.

3. Clarke states (Ann. Phil. 17, 419) that on exposing pure baryta or barium nitrate placed in a cavity made in a piece of charcoal to a burning jet of detonating gas consisting of three measures of hydrogen and one of oxygen, effervescence takes place, and white, shining little globules of metallic barium are formed.

4. Bunsen electrolysed the paste formed by mixing barium chloride with very dilute hydrochloric acid at a temperature of 100°C. in the presence of mercury, by which he obtained a solid crystalline amalgam from which the mercury was expelled by heating in a charcoal boat in a current of hydrogen. The barium thus obtained took the form of a tumefied mass, showing a silver-white lustre in the cavities (P. 91, 619).

5. Matthiessen (A. 93, 277) also obtained barium as a metallic powder by the electrolysis of the fused chloride, the negative pole consisting of a fine harpsichord wire on which the small globules of metallic barium collected, but oxidised very rapidly in air.

6. Kern (C. N. 31, 243) gives a method of preparing barium which consists in heating barium iodide with sodium, dissolving out the metallic barium with mercury, and distilling the resulting amalgam. The reaction between barium iodide and sodium is somewhat violent, being attended with evolution of heat and light.

But Donath (B. 12, 745) finds that the barium prepared by amalgamation with mercury and subsequent distillation of the mercury is not metallic barium, but is a solid amalgam containing 62-77 p.c. of mercury, which even when strongly heated in porcelain tubes does not yield the pure metal.

*Properties.*—Barium, according to Davy, is a silver-white metal; according to Clarke it has the colour and lustre of iron; Matthiessen describes it as a yellow powder; while Donath states that its true colour is that of bronze. Its melting-point is a little higher than that of iron, and its specific gravity, according to Clarke, is 4.0. It is ductile, but only slightly malleable. It oxidises rapidly in air, becoming heated, and, when sufficiently heated, burns with a dark-red light (Davy), while Clarke states that, heated in the oxyhydrogen flame, it gives out a greenish light. It decomposes water rapidly at ordinary temperatures, and is readily acted upon by sulphuric acid, with liberation of hydrogen.

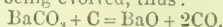
*Oxides of barium.* Two oxides of barium are known—barium oxide or baryta  $\text{BaO}$ , and barium peroxide  $\text{BaO}_2$ .

Barium oxide, protoxide, monoxide, or baryta  $\text{BaO}$  is the oxide formed when the metal burns in air. It is more readily obtained by heating (1) the nitrate or (2) the carbonate of barium.

(1) Barium nitrate is heated in a porcelain crucible or retort until no more nitrous fumes or free oxygen are given off. The heat should be carefully applied at first, otherwise, on fusing, considerable inconvenience from frothing ensues; but towards the end of the operation the heat must be raised to bright redness, and not continued too long, otherwise oxygen and carbon dioxide are absorbed from the air. The frothing may be prevented by mixing the nitrate with its own weight of barium sulphate, which is not objectionable in the product for many of the

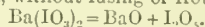
purposes to which the oxide may be put, such as the preparation of barium hydrate; this mixture with pounded heavy spar is also advisable, inasmuch as baryta attacks porcelain at high temperatures, and is thus liable to be contaminated with silica, alumina, oxide of iron, and other substances contained in the crucible; but as the mixture with sulphate does not fuse, this danger is obviated.

(2) The carbonate may also be converted into barium oxide by exposing it to the strongest heat of a forge fire; but the last traces of carbonic acid are only expelled with difficulty. However, at an ordinary white heat, this may be accomplished by mixing the carbonate with one-tenth of its weight of lamp-black or charcoal and making into a thick paste with oil or tar, carbonic oxide being evolved, thus:

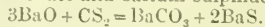


The mixture should be heated in an earthen crucible lined with lamp-black and fitted with a tight cover; on the large scale witherite is thus converted into baryta for use in separating crystallised sugar from molasses. In a second baryta-manufacturing process a mixture of the carbonates of barium and calcium is ignited in a current of aqueous vapour.

(3) On the small scale, baryta may be easily obtained by igniting barium iodate, which readily gives up all its iodine, together with five-sixths of its oxygen, without fusing or frothing:



Barium oxide as prepared by the above methods is generally a greyish-white friable mass of specific gravity 4.7-5.5. Brühlmann (A. [2] 4, 277), by heating barium nitrate in a porcelain flask, and also by using a covered porcelain crucible, obtained minute crystals of  $\text{BaO}$  belonging to the regular system, of sp.gr. 5.722.  $\text{BaO}$  is strongly alkaline, caustic, and poisonous. It is only just melted even by the heat of the oxyhydrogen blowpipe; it is a non-conductor of electricity, but in presence of mercury may be electrolysed into barium and oxygen. It is deoxidised by potassium at a red heat, and slakes with water, forming barium hydrate  $\text{Ba(OH)}_2$  with such energy that the whole mass becomes incandescent provided the amount of water be not too large. It rapidly absorbs moisture from the air. It unites with methyl and ethyl alcohols, forming the compounds  $\text{BaO} \cdot 2\text{CH}_3\text{O}$  and  $\text{BaO} \cdot 2\text{C}_2\text{H}_5\text{O}$ . Heated in the vapour of carbon disulphide, it forms barium carbonate and barium sulphide:



It dissolves readily in dilute nitric and hydrochloric acids, but with most other acids forms insoluble salts. When vapour of sulphuric anhydride is passed over it, heated to low redness in a glass tube, formation of barium sulphate  $\text{BaSO}_4$  occurs with incandescence.

Barium peroxide or dioxide  $\text{BaO}_2$  is formed when anhydrous baryta is heated to a dull red heat in a stream of oxygen or of air freed from carbonic acid. Barium hydrate may be similarly converted into the peroxide, but less readily, as it fuses below the temperature of absorption of oxygen; but the absorption may be rendered rapid by mixing the hydrate with lime or magnesia which prevents fusion and keeps the mass porous. Peroxide of barium may also be



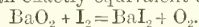
obtained by sprinkling red-hot baryta with four times its weight of powdered potassium chlorate in successive small portions; the potassium chloride simultaneously formed may be washed out with water, leaving the peroxide in the form of a hydrate.

The peroxide obtained by these means is not pure, being contaminated with a little unconverted barium oxide, iron, silica, and other substances derived from the preparing vessels. In order to purify it the finely-powdered crude product is gradually added to an excess of dilute hydrochloric acid, avoiding any considerable rise of temperature; the crude substance dissolves, forming barium chloride and peroxide of hydrogen. The solution is filtered from insoluble matters and treated with baryta water until the silica and ferric oxide, together with a little hydrated barium peroxide, regenerated by action of the peroxide of hydrogen upon the barium hydrate, are precipitated. The liquid is again filtered and then supersaturated with baryta. By this means the whole of the peroxide of hydrogen regenerates barium peroxide, which is precipitated in minute prisms or laminae of the hydrate  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ , in which condition the peroxide is best preserved, and is a suitable form for use in the preparation of peroxide of hydrogen. On drying at  $130^\circ$  or at ordinary temperatures *in vacuo* it is converted into pure anhydrous barium peroxide.

Barium peroxide is a grey, impalpable powder, slightly more fusible than the monoxide, but at a strong red heat is dissociated into oxygen and barium monoxide, and, when steam is passed over it at this temperature, forms barium hydrate. Boussingault (A. Ch. [3] 30, 5) proposes to extract oxygen from the air on an industrial scale by heating the hydrate of barium, mixed as above described with lime and magnesia, in a porcelain tube in a current of air previously freed from carbonic acid, until the whole of the oxide is converted to peroxide, then raising the temperature and passing, instead of air, vapour of water through the tube as long as oxygen continues to be given off. The monoxide of barium itself may be used instead of the hydrate, being alternately peroxidised and reduced at dull and bright redness respectively without the necessity of passing steam over it; after a few heatings the baryta loses its power of absorbing oxygen, due to a change of molecular state (A. Ch. [5] 19, 464). *In vacuo* the peroxide dissociates at a low red heat, and at this lower temperature the power of absorption is not at all injured, and the peroxidation and reduction may go on indefinitely. In 1885 a process which has since been applied with considerable success was patented by Brin (Eng. Pat. 151 and 7,867, 1885) for the manufacture of peroxide of barium for use in the preparation of oxygen and oxygenated bleaching waters. Caustic baryta is first formed by heating the dried nitrate in open crucibles to  $1,000$  to  $1,500^\circ\text{C}$ . until the contents become solid and assume a spongy appearance. The crucibles are then closed and maintained at a white heat for four hours; they are next removed to an air-tight chamber and allowed to cool in a partial vacuum so as to eliminate the nitrous fumes. The anhydrous oxide thus obtained is then heated, preferably under pres-

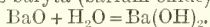
sure, in a current of air freed from moisture and carbon dioxide, and the resulting barium peroxide afterwards dissolved in acidulated water for use as a bleaching agent, or heated at a still higher temperature in steam in order to obtain the oxygen in the gaseous form.

Peroxide of barium is decomposed by sulphuretted hydrogen at ordinary temperatures, and when heated in a current of carbonic oxide it becomes white hot. It becomes incandescent when heated in sulphur dioxide. When treated with strong sulphuric acid at a temperature exceeding  $70^\circ\text{C}$ ., oxygen is given off; at lower temperatures the oxygen is mixed with ozone. When the peroxide is mixed with acidulated water in presence of oxide of silver, peroxide of manganese, or peroxide of lead, oxygen is evolved both from the peroxide of barium and from the other oxide. A small quantity of a silver compound is capable of decomposing a large quantity of barium peroxide, but iodine decomposes an exactly equivalent quantity:



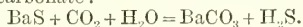
To determine the amount of active oxygen in  $\text{BaO}_2$ , Bertrand (C. N. 41, 215) proposes to add a known quantity of the peroxide to pure hydrochloric acid, add potassium iodide free from iodate together with excess of bicarbonate of soda, and titrate the liberated iodine with a standard solution of sodium thiosulphate.

**Barium hydrate, Hydrate of Baryta,** or *Caustic Baryta*  $\text{Ba}(\text{OH})_2$  or  $\text{BaO} \cdot \text{H}_2\text{O}$  is formed, with great evolution of heat, when water is added to anhydrous baryta (barium oxide):

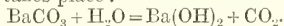


A hot concentrated solution of equivalent quantities of barium nitrate and sodium or potassium hydrate deposits, on cooling, crystals of barium hydrate. Soda is usually employed, of sp.gr.  $1.10$ – $1.15$ , and the crystals obtained are freed from mother liquor by draining, or better, by means of a centrifugal machine.

Commercial caustic baryta is now prepared on the large scale by igniting the native sulphate or heavy spar with coal or charcoal, whereby an impure barium sulphide is obtained, and heating this in earthenware retorts into which a current of moist carbonic acid is passed, thus converting it into carbonate:

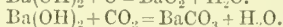
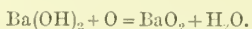


Superheated steam is then passed over the heated carbonate, when the following decomposition takes place:—



Caustic baryta crystallises from water in large, transparent, colourless, quadrate prisms capped by pyramids. The crystals  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  are isomorphous with the corresponding strontium compound. They dissolve in 20 parts of water at  $15^\circ\text{C}$ ., and in 2 parts of boiling water. The aqueous solution known as baryta water is highly caustic and of strong alkaline reaction, rapidly becoming covered with a film of carbonate owing to absorption of atmospheric carbonic acid; hence it is frequently used in the determination of the amount of carbonic acid contained in the air. On exposure to air the crystals fall to a white powder, with loss of seven molecules of water. De Forcrand (C. R. 103, 59) isolated the hydrate  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$  by allowing the compound  $\text{BaO} \cdot 2\text{CH}_3\text{O} + 2\text{H}_2\text{O}$  to evaporate

over sulphuric acid in *vacuo*. H. Lescœur (C. R. 96, 1,578) shows that at  $100^{\circ}$   $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$  has a tension of dissociation of 45 mm., and that this hydrate is completely converted to  $\text{Ba}(\text{OH})_2$  when heated to  $100^{\circ}$  in *vacuo*. The dissociation tension of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  Lescœur also proves is 213 mm. at  $75^{\circ}$ , so that at this temperature all three hydrates of  $\text{BaO}$  may exist simultaneously.  $\text{Ba}(\text{OH})_2$ , when heated alone, is only reduced to baryta above a red heat; if not heated above redness, it re-forms, on cooling, a crystalline mass of  $\text{Ba}(\text{OH})_2$ , but when heated in a current of air it takes up oxygen and is converted into peroxide of barium with loss of water; when heated in a current of carbonic acid it also loses water and is converted into barium carbonate.



Baryta has until recently been used in the processes of sugar-refining, inasmuch as it forms the compound  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{BaO}$  with cane-sugar, which, when treated with carbonic acid gas, is decomposed into insoluble barium carbonate and sugar, hence affording a means of separating the pure sugar from the molasses; but as strontium hydrate acts in a similar manner, and is not poisonous, it has been substituted for baryta in sugar-refining.

**Hydrated barium peroxide.** Schöne has shown (B. 13, 803) that only one hydrate of  $\text{BaO}_2$  exists, containing 8 molecules of water,  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ . This hydrate is precipitated in crystalline scales when peroxide of hydrogen is added to concentrated solutions of barium hydrate. It is slightly soluble in cold water, but decomposes in boiling water, forming  $\text{Ba}(\text{OH})_2$  and evolving oxygen.

**Barium chloride  $\text{BaCl}_2$ .** Crystallised (*terra ponderosa salita*)  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . Barium chloride may be prepared either from witherite, the native carbonate, or from heavy-spar, the native sulphate. The witherite is dissolved in dilute hydrochloric acid and the solution allowed to stand some time in contact with excess of the carbonate, which is added to precipitate iron and other foreign metals present in the mineral; the rapidity of precipitation is much increased by the addition of a little baryta water. The filtered liquid is then neutralised with hydrochloric acid, and the salt crystallised out and purified by recrystallisation.

From the native sulphate barium chloride may be prepared in two ways:

(1) By igniting the sulphate in a crucible with powdered coal and decomposing a filtered solution in water of the barium sulphide formed with hydrochloric acid  $\text{BaS} + 2\text{HCl} = \text{BaCl}_2 + \text{H}_2\text{S}$ .

Excess of hydrochloric acid is added, and the liquid boiled till free from sulphuretted hydrogen; it is then filtered, cooled, and evaporated to the crystallising point.

(2) By heating a mixture of 100 parts finely powdered heavy-spar, 40 parts of charcoal, 20 parts of limestone, and 50 parts of calcium chloride to a red heat in a reverberatory furnace, by which barium chloride and calcium sulphide are formed. The mass is lixiviated with water, when the barium chloride is dissolved out, leaving an insoluble calcium oxysulphide formed by

the union of the sulphide with the oxide of calcium produced by ignition of the limestone.

In this process the manganese chloride left as a by-product of the chlorine manufacture may be used in place of calcium chloride, a little sand being added along with the limestone or chalk, and the ignition being performed on a cast-iron plate. Wackenroder (D. P. J. 253, 440) has proposed to prepare barium chloride by adding an equivalent of calcium chloride to a solution of barium sulphide, and passing a stream of carbonic acid gas into the mixture, whereby calcium carbonate is precipitated.

Commercial barium chloride generally contains small quantities of strontium and calcium chlorides, together with traces of the chlorides of iron, aluminium, copper, and lead. Washing the crystals with alcohol removes both the strontium and calcium chlorides, while calcium chloride may also be removed by digesting with barium carbonate suspended in water, when the calcium chloride becomes converted to carbonate, or more rapidly by adding baryta water and passing carbonic acid gas into the liquid. Digestion with barium carbonate also precipitates the sesquioxides of iron and alumina. Lead and copper may best be removed by the addition of a little barium sulphide.

Barium chloride may be recovered from mixtures of chlorides of the alkalis and alkaline earths by treating the concentrated liquor with a hot saturated solution of salt, when on cooling a mixture of barium and sodium chlorides crystallises out; by treating a cold saturated solution of this mixture with twice its volume of hydrochloric acid, barium chloride is precipitated (D. P. J. 250, 91).

Barium chloride crystallises from aqueous solution with two molecules of water  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in transparent, colourless, rhombic tables. Specific gravity 2.66-3.05. The crystals decrepitate when heated. They have an unpleasant, bitter, sharply saline taste, exciting nausea, and are very poisonous.

One hundred parts of water at  $0^{\circ}\text{C}$ . dissolve 32.62 parts of anhydrous barium chloride, and 0.2711 parts for every degree above  $0^{\circ}\text{C}$ .; 100 parts of water at  $15.6^{\circ}$  dissolves 43.5, and at  $105.5^{\circ}$  78 parts of the crystallised chloride. One part of crystallised barium chloride at  $18.1^{\circ}$  dissolves in 2.257 parts of water to form a solution of specific gravity 1.28251 (Karsten). A solution saturated at  $8^{\circ}$  has a specific gravity of 1.270 (Anthon).

Barium chloride is almost insoluble in strong hydrochloric acid, so that it is precipitated from its solutions by hydrochloric acid, and a few drops of the acid reduces the solubility considerably. Hot absolute alcohol dissolves only  $\frac{1}{1000}$  part of the crystals; but according to Fresenius, 1 part of the salt dissolves in 8,108 parts of alcohol of 99.3 p.c. at  $14^{\circ}\text{C}$ ., and in 1,857 parts of the same alcohol at its boiling point.

The crystals are not efflorescent, but give up the whole of their water at  $100^{\circ}\text{C}$ ., leaving a white mass of the anhydrous salt, which melts at a red heat, forming a translucent mass on cooling. Specific gravity of the anhydrous chloride is given by various observers as 3.70 to 4.15. When heated in a current of steam it evolves hydrochloric acid below its fusing point.

A concentrated solution of barium chloride is decomposed by sodium or potassium nitrate forming barium nitrate and a chloride of the alkali-metal. With glycochol  $\text{CH}_2(\text{NH}_2)\text{COOH}$  it forms a crystalline compound, and also acts upon blood as a preventive of putrefaction and coagulation.

Barium chloride is extensively used as a reagent, especially for the detection and estimation of sulphuric acid. It is also used for the preparation of artificial sulphate or 'permanent white,' and for preventing the incrustation of steam boilers by decomposing the gypsum of hard waters.

**Barium oxychloride.** André (C. R. 93, 58) obtained an oxychloride of barium by adding 60 grams of  $\text{Ba}(\text{OH})_2$  to 200 grams of crystallised barium chloride, and boiling the mixture with 500 grams of water, filtering, and allowing to cool, when nacreous lamellae, to which he (C. R. 98, 572) ascribed the formula  $\text{BaCl}_2 \cdot \text{BaO} \cdot 5\text{H}_2\text{O}$ , separated out. Beckmann (J. pr. [2] 27, 126) also obtained nacreous plates by similar means to which he gave the formula  $\text{BaCl}(\text{OH}) \cdot 2\text{H}_2\text{O}$ . These plates lose  $\frac{2}{3}$ ths of their water at  $120^\circ$  and the remaining fifth at the fusing point by prolonged heating in a stream of hydrogen. This oxychloride is readily decomposed by water and alcohol.

**Barium chlorate**  $\text{Ba}(\text{ClO}_3)_2$ . Dry  $\text{Ba}(\text{OH})_2$  does not absorb chlorine, but in presence of water it rapidly takes it up, forming first hypochlorite and chloride, the former of which breaks up into chlorate and chloride

$6\text{BaO} + 6\text{Cl}_2 = 5\text{BaCl}_2 + \text{Ba}(\text{ClO}_3)_2$   
(Konigsel-Weisberg, B. 12, 346).

As it is difficult to separate from the chloride, the chlorate is best prepared by neutralising a solution of chloric acid with barium carbonate and evaporating to the crystallising point. It crystallises in colourless monoclinic prisms with 1 molecule of water, soluble in 4 parts of cold and less than 1 part of boiling water.

Barium chlorate is also slightly soluble in alcohol, and the alcoholic solution burns with a green flame.

If strongly heated fused barium chlorate be plunged into a jar of coal gas, a brilliant combustion of the carbon and hydrogen contained in the coal gas occurs at the expense of the oxygen of the chlorate.

**Barium perchlorate**  $\text{Ba}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$  is readily formed by neutralising perchloric acid with barium hydrate or carbonate. It crystallises from the solution in long deliquescent prisms, very soluble in water.

**Barium bromide**  $\text{BaBr}_2$ . Crystallised  $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ .

This salt is prepared by saturating baryta water or barium carbonate or sulphide with hydrobromic acid; or by decomposing the sulphide with free bromine, sulphur being precipitated.

The most convenient method is to bring together under water 12.5 parts of bromine and 1 part of amorphous phosphorus, by which a solution of hydrobromic and phosphoric acids is formed, which is neutralised with barium carbonate rendered alkaline by baryta water. The insoluble barium phosphate may then be filtered off and the bromide obtained by evaporation and crystallisation.

Barium bromide is very soluble in water, and crystallises with difficulty; it is isomorphous with the chloride, but unlike the latter salt is soluble in strong alcohol. It loses one molecule of water at  $75^\circ$ , and the second at  $120^\circ$  (Beckmann, J. pr. [2] 27, 126).

**Barium oxybromides.** Two oxybromides have been prepared by Beckmann (*l.c.*).

$\text{BaBr}(\text{OH}) \cdot 2\text{H}_2\text{O}$  resembles the corresponding oxychloride.  $\text{BaBr}(\text{OH}) \cdot 3\text{H}_2\text{O}$  was obtained by adding alcohol to mixed solutions of  $\text{BaBr}_2$  and  $\text{Ba}(\text{OH})_2$ .

**Barium iodide**  $\text{BaI}_2$ . Crystallised  $\text{BaI}_2 \cdot 7\text{H}_2\text{O}$ . Barium iodide is formed when hydriodic acid gas is passed over baryta at a red heat, a violent action occurring attended with incandescence. It is generally prepared by mixing barium monosulphide with a saturated solution of iodine in alcohol as long as sulphur is precipitated; the filtrate is then boiled rapidly to near dryness, redissolved in a little water and again evaporated, this time to dryness, preventing the access of air as much as possible by performing the operation in a glass bolt-head. On redissolving the mass in hot water and allowing to cool, slender needles separate out of the composition  $\text{BaI}_2 \cdot 7\text{H}_2\text{O}$  (Croft, G. 1856, 125; Thomsen, B. 10, 1,343).

These crystals are very deliquescent and readily soluble in alcohol. They lose 6 molecules of water at  $125^\circ$ , and the remainder at  $150^\circ$  (Beckmann, J. pr. [2] 27, 126). They decompose slowly at ordinary temperatures, and quickly when warmed, giving off violet vapours of iodine.

The double iodide of barium and mercury has a specific gravity of 3.588 higher than that of Thoulet's solution, and may be of use for petrographic purposes (Rohrbach, J. M. 1883, 2, Mem. 186).

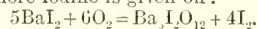
**Barium oxyiodide.** Beckmann (J. pr. [2] 27, 126) also prepared an oxyiodide of barium of the formula  $\text{BaI}(\text{OH}) \cdot 4\text{H}_2\text{O}$  which crystallises in short thick needles.

**Barium iodate**  $\text{Ba}(\text{IO}_3)_2$  is largely used for the preparation of iodic acid, and is obtained as a white granular precipitate by adding potassium iodate to barium chloride.

It is soluble in 3,000 parts of cold and 600 parts of boiling water. It dissolves in hot nitric acid, and crystallises out on cooling in bright, glittering, monoclinic prisms isomorphous with the chlorate. Hydrochloric acid dissolves it with evolution of chlorine.

**Barium periodate.** By passing iodine vapour in a current of dry air over heated oxide of barium a basic periodate of the formula  $\text{Ba}_3\text{I}_2\text{O}_{12}$  or  $\text{Ba}(\text{IO}_3)_2 \cdot 4\text{BaO}$  is formed. The same basic periodate is formed when barium iodate is heated to a high temperature:

$5\text{Ba}(\text{IO}_3)_2 = \text{Ba}_3\text{I}_2\text{O}_{12} + 4\text{I}_2 + 9\text{O}_2$   
or on heating iodide of barium in a current of air until no more iodine is given off:



Hence Sugiura and Cross (C. J. 1879, 118) conclude that  $\text{Ba}_3\text{I}_2\text{O}_{12}$  is the most stable combination of barium, iodine, and oxygen.

**Barium fluoride**  $\text{BaF}_2$  is obtained by neutralising hydrofluoric acid with barium hydrate or recently precipitated carbonate; or by precipitating a solution of barium nitrate with sodium or potassium fluoride. It forms a white, granular, crystalline powder, sparingly soluble in water,



but readily soluble in nitric, hydrochloric, or hydrofluoric acids.

It combines with fluorides of silicon and boron, forming the compounds  $\text{BaF}_2 \cdot \text{SiF}_4$ , barium silicofluoride and  $\text{BaF}_2 \cdot 2\text{BF}_3$ . The former is precipitated by adding hydrofluosilicic acid to soluble barium salts as a crystalline precipitate totally insoluble in alcohol, and serves as a means of separating barium from strontium and calcium, which are not precipitated by hydrofluosilicic acid.

Barium fluoride forms a crystalline compound with the chloride of barium  $\text{BaCl}_2 \cdot \text{BaF}_2$  when a solution of barium chloride is mixed with one of sodium or potassium fluoride; this double compound is more stable than the fluoride itself, and remains as a granular mass on evaporation of the solution.

**Barium carbonate**  $\text{BaCO}_3$ . The native carbonate was first noticed to occur at Leadhills in Scotland, in 1783, by Withering, and hence received the name *witherite*. It is found in many places in England, specially fine crystals being met with at Fallowfield in Northumberland; it is also found in Silesia, Hungary, Styria, Russia, South America. Witherite crystallises in the rhombic system isomorphous with aragonite, the crystals being generally prismatic owing to the predominance of the faces  $\alpha P$ ,  $\alpha P\infty$  and  $P\infty$ . It occurs also in globular, tuberoso, and botryoidal forms; also amorphous. Sp.gr. 4.29-4.35, hardness 3 to 3.75, lustre vitreous to resinous, colour white to grey, streak white. Subtransparent to translucent; fracture uneven; brittle.

Knop (Landw. Versuchs-Stat. 17, 65) found 0.02 p.c. of barium carbonate in Nile mud from Minich and Achmin; and Dworzak (Landw. Versuchs-Stat. 17, 65) found baryta in the ash of the wheat grown thereon. *Alstonite* ( $\text{BaCaCO}_3$ ) contains barium and calcium in varying proportions, and is isomorphous with witherite. *Baryto-calcite*  $\text{BaCO}_3 + \text{CaCO}_3$  crystallises in the monoclinic system.

Barium carbonate is rapidly formed when baryta, hydrated or anhydrous, is exposed to the atmosphere. When  $\text{BaO}$  is strongly heated it absorbs  $\text{CO}_2$ , becoming incandescent; but the carbonate is not formed at this temperature (Raoult, C. R. 92, 1, 110).

It is readily prepared by precipitating aqueous solutions of the nitrate or chloride with ammonium carbonate, filtering, and washing with hot water; or by igniting a mixture of 10 parts powdered heavy-spar, 2 parts charcoal, and 5 parts pearl ash (potassium carbonate). Potassium sulphide and barium carbonate are obtained and may be separated by water. The impure carbonate thus produced may be used to prepare other salts of barium, but these salts will contain iron.

Artificial barium carbonate is a dense soft white powder, poisonous and hence used for destroying rats. It is very sparingly soluble in water, slightly soluble in water containing carbonic acid, owing to the formation of an acid carbonate which is stable only in solution. It dissolves readily in ammonium chloride, nitrate, and succinate, and when boiled with ammonium chloride is totally decomposed, forming ammonium carbonate and barium chloride.

It is not decomposed at a strong red heat, but at the heat of a forge fire it fuses with loss of carbon dioxide; the decomposition is much more easily effected in presence of carbon. It is decomposed by steam at a red heat, and very easily if mixed with an equal weight of chalk or slaked lime.

The artificial carbonate is of considerable use in chemical analysis.

**Barium nitrite**  $\text{Ba(NO}_2)_2 \cdot \text{H}_2\text{O}$  is prepared by igniting the nitrate at a moderate heat, dissolving in water, and precipitating any baryta formed by passing a stream of carbonic acid gas through the solution, adding alcohol to the filtrate to precipitate the unreduced nitrate, and evaporating to the crystallising point. Or by passing nitrous vapours into baryta water, evaporating to dryness, digesting in a small quantity of water (not sufficient to dissolve the nitrate) and crystallising. It is most readily prepared pure by adding barium chloride to a boiling solution of silver nitrite, filtering off the silver chloride and evaporating.

It is permanent in the air, readily soluble in water and alcohol, and crystallises in colourless prisms, either needle-shaped or thick short prisms of  $71^\circ$ , according to Fischer.

**Barium nitrate**  $\text{Ba(NO}_3)_2$ . A native barium nitrate has been discovered in Chili in the form of colourless octahedra, occasionally twinned like spinelle (Groth, J. M. 1883, 1, Ref. 14).

Barium nitrate is prepared on the large scale either by dissolving the native carbonate (witherite) or the crude sulphide in dilute nitric acid, or by mixing hot saturated solutions of barium chloride and sodium nitrate. On cooling, the larger portion of the barium nitrate crystallises out, and the evaporation of the mother liquors yields the remaining portion.

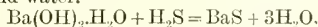
Barium nitrate crystallises in lustrous, colourless, regular octahedra, frequently modified by faces of the cube, of specific gravity 3.2. The crystals are permanent in the air, decrepitating when heated and melting at  $597^\circ$  (Carnelley). At a red heat the salt decomposes, evolving oxygen, nitrogen, and nitrogen peroxide, and leaving a residue of pure baryta. It detonates slightly with combustible bodies, and decomposes with a yellowish light when thrown upon the fire. It is largely used in pyrotechny for giving green coloured lights, especially for the preparation of green fire; and for the manufacture of *saxifragin*, an explosive mixture of 76 parts of barium nitrate, 2 parts of nitre, and 22 parts of charcoal.

It dissolves in water, producing a slight depression of temperature; 100 parts of water dissolve 5.2 parts of barium nitrate at  $0^\circ\text{C}$ ., 9.2 at  $20^\circ\text{C}$ ., 17.1 at  $50^\circ\text{C}$ ., and 32.2 at  $100^\circ\text{C}$ . It is less soluble in dilute nitric acid; hence a second crop of crystals may be obtained from cooled saturated solutions on addition of a little nitric acid. It is quite insoluble in concentrated nitric acid and in alcohol.

Hlirzel (Zeitschr. f. Pharm. 1854, 49) obtained a hydrate  $\text{Ba(NO}_3)_2 \cdot 2\text{H}_2\text{O}$  from a solution cooled to between  $0^\circ$  and  $12^\circ$ . Berry (C. N. 44, 190), by saturating the same water with barium and strontium nitrates, introducing a crystal of  $\text{Sr(NO}_3)_2 \cdot \text{H}_2\text{O}$ , and evaporating over sulphuric acid in vacuo, obtained crystals containing 17

per cent. of a hydrated barium nitrate isomorphous with the strontium compound.

**Barium monosulphide**  $\text{BaS}$  is obtained in a pure state by passing sulphuretted hydrogen over heated baryta as long as water is formed. Veley (C. J. 1886, 369) prepared pure crystals of the hydrate of barium hydroxide  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and heated them at  $80^\circ$  in a current of hydrogen until they attained the constant composition  $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , when a stream of sulphuretted hydrogen was passed over them, yielding pure  $\text{BaS}$  and water.

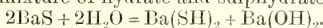


It may also be prepared by passing carbon bisulphide over red-hot baryta or by reducing powdered barium sulphate in a stream of hydrogen.

On the manufacturing scale it is prepared by roasting 100 parts of heavy-spar with 20 parts of coal slack or charcoal. If charcoal is used a thorough mixture must be effected, as the reaction is otherwise very imperfect owing to the non-fusibility of the mass. If the slack of bituminous coal is used, the 'caking' supplies a carbonaceous material which readily permeates the mass and insures complete reduction. The admixture of resin, oil, or sawdust is also advantageous, and the asphalt of gas-works is a capital reducing material, as the hydrogen contained in it prevents the formation of polysulphides of barium. The mass thus obtained contains excess of carbon and some undecomposed sulphate, but the barium sulphide may be extracted by treating with hot water.

Another method is to heat a mixture of 100 parts heavy-spar, 200 of common salt, and 15 parts charcoal powder in a reverberatory furnace, the salt being added to assist fusion.

Barium sulphide forms a white mass of hepatic odour and alkaline taste, soluble in water, forming a mixture of hydrate and sulphhydrate



When exposed to the air it becomes converted into carbonate with evolution of sulphuretted hydrogen, owing to absorption of moisture and carbonic acid. When heated to redness in presence of aqueous vapour, it is converted into barium sulphate with elimination of hydrogen. It is decomposed by hydrochloric and nitric acids with formation of the chloride and nitrate and elimination of sulphuretted hydrogen. Chlorine, bromine, and iodine decompose it with formation of chloride, bromide, and iodide, and deposition of sulphur.

The phosphorescent material known as 'Bolognian phosphorus' is a sulphide of barium obtained by heating 5 parts of precipitated barium sulphate with 1 part of powdered charcoal over a gas flame for half an hour, and then igniting for ten minutes over the blowpipe; it must be sealed up while still hot in glass tubes. After exposure to the sun's rays, or to any light rich in ultra-violet rays such as that emitted by burning magnesium wire or the electric arc, it phosphoresces in the dark with a brilliant orange-coloured light. Sulphides of barium, strontium, and calcium are now manufactured for the preparation of luminous paints which are used for coating clock-faces, match-boxes, &c. Their surfaces are protected from moisture by a thin coating of varnish.

When a solution of 5 parts of barium sulphide is boiled with 1 part of sulphur and the solution evaporated over sulphuric acid *in vacuo*, colourless six-sided transparent tables of  $\text{BaS} + 6\text{H}_2\text{O}$  are deposited, which are decomposed by a small quantity of water forming barium hydrosulphide which dissolves and barium hydroxide which remains behind.

**Barium hydrosulphide**  $\text{Ba}(\text{SH})_2$  is formed by saturating a warm solution of barium hydrate or sulphide with sulphuretted hydrogen, evaporating apart from the air and cooling, when crystals of baryta and yellow prisms separate out. The mother liquor is mixed with alcohol, filtered from the sulphur and barium thiosulphate formed, and cooled to  $-10^\circ\text{C}$ , when colourless transparent four-sided prisms are obtained. The crystals contain water, which they lose on heating, becoming white. Exposure to air decomposes the crystals, with efflorescence, into barium thiosulphate and sulphate. Heated in a retort they lose their water of crystallisation without fusing, evolving sulphuretted hydrogen as the temperature approaches redness and leaving a yellow mass of barium monosulphide, which becomes white on cooling. It is insoluble in alcohol.

Veley (C. J. 1886, 369) finds that the composition of crystals of barium sulphhydrate is  $\text{Ba}(\text{SH})_2 \cdot 4\text{H}_2\text{O}$ .

**Barium trisulphide**  $\text{BaS}_3$  is formed when 2 parts of barium sulphide are fused with 1 part of sulphur, the excess of sulphur being distilled off below  $360^\circ$ , as a greenish-yellow mass. It melts at  $400^\circ$  with loss of sulphur and formation of a black liquid. On boiling for some time with water it dissolves to a red liquid which deposits on cooling crystals of the hydrated mono- and tetrasulphides of barium.

**Barium tetrasulphide**  $\text{BaS}_4$ . When 7 parts of barium sulphide are boiled in water with 4 parts of sulphur, pale red rhombic prisms are deposited, soluble in water to a red-coloured liquid from which alcohol precipitates it as an orange-coloured crystalline powder.

Veley (C. J. 1886, 369) obtains it by dissolving sulphur in a warm saturated solution of barium hydrosulphide; the crystals which separate out have the composition  $\text{BaS}_4 \cdot 2\text{H}_2\text{O}$ .

**Barium pentasulphide**  $\text{BaS}_5$  is obtained in solution by boiling an aqueous solution of the monosulphide with sulphur. On evaporation of the caustic alkaline yellow solution, crystals of barium tetrasulphide and sulphur are obtained:  $\text{BaS}_5 = \text{BaS}_4 + \text{S}$ .

**Barium sulphocarbonate**  $\text{BaCS}_3$  is deposited as a canary-yellow crystalline powder when a solution of barium sulphide is added to carbon bisulphide (Thenard, C. R. 79, 673). On the large scale 90 p.c. yield may be obtained, and Dumas has suggested its use against the phylloxera in wine districts. Thenard is of opinion that this barium salt would be injurious to the soil and proposes to convert it into the potassium salt by adding potassium sulphate to its solution.

**Barium sulphite**  $\text{BaSO}_3$  is obtained as a white crystalline precipitate by adding potassium or sodium sulphite to a soluble barium salt. Soluble in a warm solution of sulphurous acid, and crystallises out on cooling in six-sided prisms.

When heated in closed vessels it is converted into a mixture of sulphide and sulphate, but heated in air the sulphate is the sole product. Birnbaum and Wittich (B. 13, 651) state that BaO unites slowly with  $\text{SO}_2$  at  $200^\circ$ , but more rapidly at  $230^\circ$ , forming  $\text{BaSO}_3$ .

**Barium sulphate**  $\text{BaSO}_4$  occurs very largely as *barytes* or *heavy-spar*, often in distinct veins, and frequently forming fine rhombic crystals, generally associated with sulphides of the metals of the antimony, mercury, and manganese groups; as these sulphides are mostly volatile, Vieulafait (C. R. 97, 51) concludes that barytes can never have been subjected to even a moderately high temperature. Clowes (C. N. 52, 194) states that the beds of the new red sandstone near Nottingham are permeated by minute crystals of heavy-spar which acts as a cementing material.

Crystals of artificial barytes, identical in form and properties with native heavy-spar may be obtained by fusing certain metallic chlorides, such as those of manganese, sodium, potassium, or even barium itself, gradually dissolving barium sulphate in the fused mass, very slowly cooling, and afterwards extracting the soluble chlorides with water. By this means Gorgeu (C. R. 96, 1,734) prepared crystals much larger than those obtained by the older process of fusing potassium sulphate with barium chloride. The specific gravity of the mineral and of the artificial crystals varies from 4.3 to 4.7.

Barium sulphate has been formed by Spring (Bl. 46, 299) by subjecting an intimate mixture of molecular proportions of sodium sulphate and barium carbonate to great pressure. It is precipitated as a heavy white amorphous powder of specific gravity 4.0-4.5, whenever sulphuric acid or a soluble sulphate is added to the solution of a barium salt; this precipitate is insoluble in water, very slightly soluble in dilute acids, more so in strong acids. Concentrated sulphuric acid does not attack anhydrous baryta, but pyrosulphuric acid attacks it so violently that the mass becomes incandescent and forms barium sulphate. When freshly precipitated it is readily soluble in concentrated sulphuric acid at  $100^\circ$ , the solution depositing on cooling lustrous prisms of the *acid barium sulphate*  $\text{BaH}_2(\text{SO}_4)_2$ . If the acid solution be exposed to the air, moisture is taken up, and silky needles of a salt having the composition  $\text{BaH}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  are deposited. Both these acid salts are decomposed by water, yielding sulphuric acid and the neutral salt.

Barium sulphate is also soluble to a perceptible extent in ammonium nitrate. Hydrobromic acid solution containing 40 p.c. HBr dissolves it to the extent of 1 in 2,500 parts acid (Haslam, C. N. 53, 87).

Barium sulphate is partially decomposed by boiling with a concentrated solution of a fixed alkaline carbonate into alkaline sulphate and barium carbonate, but the reaction is much more complete when the sulphate and alkaline carbonate are fused together. It is reduced to sulphide by ignition with charcoal or organic matter, also by ignition in a stream of coal gas or of hydrogen mixed with vapour of carbon bisulphide.

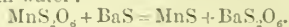
Powdered heavy-spar is used to adulterate white lead, but has not sufficient body to form a

pigment by itself; the amorphous sulphate is prepared on the large scale by precipitation of a solution of barium chloride of sp.gr. 1.19 by one of sulphuric acid of sp.gr. 1.245, and is used as a pigment under the name of 'permanent white' or 'blanc fixe.'

**Barium sodium sulphate**  $\text{BaNa}_2(\text{SO}_4)_2$  is formed as an opaque hard mass of pearly lustre by fusing together equivalent quantities of the sulphates of sodium and barium (Berthier).

**Barium disulphate**  $\text{BaS}_2\text{O}_6$ . If precipitated barium sulphate be dissolved in fuming sulphuric acid, and the solution heated to  $150^\circ$ , on cooling a glistening deposit of granular crystals of the disulphate is obtained. Decomposition of these crystals occurs at a low red heat without previous fusion.

**Barium dithionate**  $\text{BaS}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ . Prepared by adding barium sulphide to the manganese salt formed on passing sulphurous anhydride through finely divided manganese dioxide suspended in water:



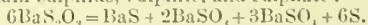
On allowing the solution to evaporate in a warm place, glittering monoclinic crystals of the salt are deposited of the composition  $\text{BaS}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ . According to Sénarmont and Rammelsberg the crystals are rhombic. According to V. Lang (Sitz. B. [2] 45, 27), they are monoclinic.

The crystals are soluble in 4 parts of water at  $18^\circ\text{C}$ . and in 1.1 parts at  $100^\circ$ . When the dry salt is ignited it breaks up into sulphur dioxide and barium sulphate. The same decomposition occurs on boiling with hydrochloric acid, but the solution of the dithionate itself in water may be boiled without decomposition.

A tetrahydrate  $\text{BaS}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$  may also be obtained by spontaneous evaporation in distinct shining monoclinic crystals, which effloresce on exposure to air.

**Barium thiosulphate**  $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$  or  $\text{BaH}_2(\text{SO}_3)_2$

is obtained as a white crystalline precipitate when the sodium salt  $\text{Na}_2\text{S}_2\text{O}_3$  is added to barium acetate; loses its water of crystallisation at  $215^\circ$ . The anhydrous salt when heated to redness gives off sulphur and leaves a residue of barium sulphide, sulphite, and sulphate:



**Barium selenide**  $\text{BaSe}$  is formed by heating barium selenite to redness in a stream of hydrogen. It is decomposed by water into barium hydrate and a higher selenide, which is decomposed by acids with evolution of  $\text{H}_2\text{Se}$  and precipitation of selenium.

**Barium selenate**  $\text{BaSeO}_4$  resembles the sulphate in being insoluble in water, but differs from it in being decomposed by hydrochloric acid into selenite, which dissolves in the hydrochloric acid.

**Barium chromate**  $\text{BaCrO}_4$  is precipitated as a yellow crystalline powder when potassium chromate or bichromate is added to the solution of a barium salt. The salt may be obtained in green rhombic crystals isomorphous with  $\text{BaSO}_4$  by heating two equivalents of  $\text{BaCl}_2$  with one equivalent of potassium chromate and one of sodium chromate, and allowing the mixture to cool; the chlorides may be boiled out with water, leaving the right rhombic prisms of  $\text{BaCrO}_4$  of sp.gr. 4.6. They are insoluble in water, but



are easily soluble in hydrochloric and nitric acids, and are decomposed by sulphuric acid into  $\text{BaSO}_4$  and  $\text{CrO}_3$  (Bourgeois, C. R. 88, 382).

The precipitated chromate is used as a pigment under the name of 'lemon yellow' or 'yellow ultramarine.' When strong sulphuric acid is added to the dry pigment great heat is developed, and it is coloured deep red from liberation of  $\text{CrO}_3$ . If it be now ground in a mortar and heated to bright redness, the chromic acid is reduced to chromic oxide and a fine green pigment is obtained (Douglas, C. N. 40, 59).

**Barium dichromate**  $\text{BaCr}_2\text{O}_7$  is obtained by dissolving barium chromate in hot concentrated chromic acid. On cooling, red crystals of the composition  $\text{BaCr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  are deposited, which lose their water at  $100^\circ$ , and are decomposed by water into the normal chromate and chromic anhydride (Preis and Rayman, B. 13, 340).

**Barium manganate**  $\text{BaMnO}_4$  is formed when manganese dioxide is heated with barium carbonate or nitrate as an emerald-green powder consisting of microscopic four-sided prisms or six-sided plates, insoluble in water but decomposed by acids. This salt is now used in place of the poisonous Scheele's green.

**Barium permanganate**  $\text{BaMn}_2\text{O}_8$  is prepared by passing carbonic acid gas through water containing barium manganate in suspension; after filtering off the barium carbonate the red solution is rapidly evaporated. Or it may be obtained by the action of barium chloride on silver permanganate.

Or potassium permanganate may be decomposed by slight excess of hydrofluosilicic acid, the mixture kept cool, and, after separation of the precipitated potassium silicofluoride, the supernatant solution decanted and saturated in the cold with barium hydrate. After separation of the insoluble barium silicofluoride, the solution is evaporated until the barium permanganate separates out on cooling (Rousseau and Bruneau, C. R. 98, 229).

It forms large orthorhombic octahedra, deep red and almost black, with a violet reflection.

It is used for the preparation of permanganic acid and of the ammonium salt.

Rousseau and Saglier (C. R. 99, 139) find that on heating two grams of barium manganate with ten grams of barium chloride for four hours to  $1,500^\circ\text{C}$ ., and extracting with water and dilute acid, a residue of small opaque bluish-black crystals of *barium manganite*  $\text{BaMnO}_3$  remains, sp.gr. 5.85, readily soluble in hydrochloric acid with evolution of chlorine. The manganite is also formed when mixtures of manganese chloride and barium oxychloride are heated to a temperature below  $1,000^\circ\text{C}$ . or above  $1,100^\circ\text{C}$ . Between these temperatures the product is barium dimanganite  $\text{BaO} \cdot 2\text{MnO}_2$  which crystallises in brilliant black lamellae. At  $1500^\circ\text{C}$ . the manganite is reconverted to manganate.

**Barium phosphide.** When vapour of phosphorus is passed over red-hot baryta a brownish-red mixture of barium phosphide and phosphate is obtained commonly known as 'phosphuret of baryta,' the reaction being said to be as follows:  $-8\text{BaO} + 12\text{P} = 5\text{BaP}_2 + \text{Ba}_3(\text{PO}_4)_2$ .

It is decomposed by water, forming a solution of hypophosphite of barium and evolving a

mixture of free hydrogen and spontaneously inflammable phosphoretted hydrogen.

**Barium mono-metaphosphate** is obtained as a white powder by evaporating a solution of barium carbonate in excess of metaphosphoric acid and heating the residue to  $316^\circ$ . Its formula is not known with certainty.

**Barium dimetaphosphate**  $\text{Ba}(\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$  is formed as a crystalline sparingly soluble precipitate when barium chloride is added to a solution of the corresponding ammonium or sodium salt.

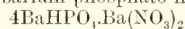
**Barium trimetaphosphate**  $\text{Ba}_3\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ , apparently a polymeric form of the last salt, is produced when a solution of 1 part of the corresponding sodium salt in 10 to 15 parts of water is mixed with a nearly saturated solution of 3 parts barium chloride. On standing the salt separates in monoclinic prisms, which give off two-thirds of their water at  $100^\circ$ , and the rest at a higher temperature.

**Barium hexametaphosphate** is obtained as a gelatinous precipitate by precipitating the corresponding sodium salt with barium chloride.

**Monobarium orthophosphate**  $\text{BaH}_2(\text{PO}_4)_2$  is prepared by evaporating a solution of the di- or tri-barium salt in aqueous phosphoric acid. It forms colourless crystals—triclinic according to Erlenmeyer, with acid reaction; soluble without decomposition in a small quantity of water, but decomposed by excess of water into free phosphoric acid and the neutral salt.

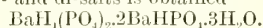
Joly (C. R. 98, 1274) states that as the total weight of salt brought in contact with the same quantity of water increases in arithmetical progression, the weight which is dissolved without decomposition decreases in geometrical progression; but as soon as half the original salt has been decomposed a diacid salt is formed  $\text{BaO} \cdot 2\text{P}_2\text{O}_5 + x\text{H}_2\text{O}$ , the proportion of which increases as the acidity of the liquid increases, and eventually exists alone in solution.

**Dibarium orthophosphate**  $\text{Ba}_2\text{H}_2(\text{PO}_4)_2$  or  $\text{BaHPO}_4$  is obtained as a white, scaly, crystalline precipitate when hydrogen disodium phosphate is added to a neutral solution of a barium salt. It is soluble in 20,570 parts of water at  $20^\circ$ , somewhat more soluble in water containing barium or sodium chloride or ammoniacal salts. From the solution in nitric or hydrochloric acid excess of ammonia precipitates the tribarium salt or a salt intermediate between the two. Thus, according to Wackenroder, a solution of  $\text{BaHPO}_4$  in nitric acid yields, on addition of ammonia, a precipitate of barium phosphato-nitrate



which leaves, on ignition, a mixture of di- and tribarium phosphates.

By precipitating a solution of dibarium phosphate with alcohol a salt intermediate between the mono- and di-salts is obtained



If a mixture of potassium silicate and baryta water is boiled, and afterwards mixed with a solution of potassium silicate containing a quantity of potassium phosphate, on cooling, cubical crystals of the composition  $\text{BaKPO}_4 \cdot 10\text{H}_2\text{O}$  separate out.  $\text{BaNaPO}_4 \cdot 10\text{H}_2\text{O}$  was similarly obtained in regular tetrahedrons (De Schulten C. R. 96, 706).

**Tribarium orthophosphate**, or neutral phosphate of barium,  $\text{Ba}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  is prepared by

adding hydrogen disodium phosphate to a solution of barium chloride rendered strongly alkaline by ammonia, and separates as a heavy granular powder. It parts with a portion only of its water at 200°C.

If a saturated solution of tribarium phosphate in hydrochloric acid is evaporated, on cooling, crystals of barium chloride are deposited, more and more monobarium phosphate being left in solution, and if more hydrochloric acid is added, all the barium may be crystallised out as barium chloride and pure phosphoric acid remains.

If the solution of tribarium phosphate in hydrochloric acid is boiled, shining needles form in the liquid, and on adding sufficient water to redissolve them, well-defined crystals of a phosphato-chloride  $4\text{BaH}_4(\text{PO}_4)_2 \cdot \text{BaCl}_2$  are deposited on standing (Erlenmeyer, J. 1857, 147).

According to Ludwig, a solution of dibarium phosphate in hydrochloric acid also yields, on addition of ammonia, a phosphato-chloride containing  $3\text{Ba}_2\text{H}_2\text{P}_4\text{O}_{16} \cdot \text{BaCl}_2 \cdot 3\text{H}_2\text{O}$ .

A salt intermediate between the di- and tri-phosphates, containing  $\text{Ba}_3(\text{PO}_4)_2 \cdot 2\text{BaHPO}_4$  or  $\text{Ba}_4\text{H}_2\text{P}_4\text{O}_{16}$ , is formed when a solution of the dibarium phosphate in hydrochloric acid is mixed with a quantity of ammonia just sufficient to precipitate it.

**Barium pyrophosphate**  $\text{Ba}_2\text{P}_2\text{O}_7$ . Pyrophosphoric acid does not precipitate barium salts, but with baryta water gives a precipitate of barium pyrophosphate. Barium salts, however, give with sodium pyrophosphate a white amorphous precipitate of barium pyrophosphate, soluble in aqueous pyrophosphoric and sulphurous acids; more soluble in hydrochloric or nitric acid, but not perceptibly soluble in water containing ammonium chloride or in acetic acid.

**Monobarium arsenate**  $\text{BaH}_2(\text{AsO}_4)_2$  is obtained by adding baryta water to aqueous arsenic acid until a precipitate begins to form, or by dissolving the dibarium salt in aqueous arsenic acid and leaving the solution to crystallise.

**Dibarium arsenate**  $2\text{BaHAsO}_4 \cdot \text{H}_2\text{O}$ , or



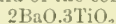
according to Berzelius, is obtained when a solution of the disodium salt is added to excess of barium chloride. It gives up its water at a red heat, and in contact with water is decomposed into the tribarium salt, which is precipitated, and the monobarium salt, which dissolves.

**Tribarium arsenate**  $\text{Ba}_3(\text{AsO}_4)_2$  is obtained as a white sparingly soluble powder by precipitating aqueous arsenic acid with baryta water, or better, by gradually dropping trisodium arsenate into barium chloride.

**Barium silicate.** Solutions of baryta, when kept in glass bottles for any length of time deposit transparent rhombic crystals of the composition  $\text{BaSiO}_3 \cdot 7\text{H}_2\text{O}$ . These crystals lose their water a little above 100° and become turquoise-blue; they are decomposed by boiling water (Le Chatelier, C. R. 92, 931); Cossa and Lavallo (Z. 11, 399).

According to Le Chatelier they may be readily obtained in a few days, by suspending calcined silica in baryta water, when the sides become covered with crystals.

**Barium titanate.** When equivalent quantities of titanio anhydride and barium carbonate are fused at a bright red heat for an hour with excess of barium chloride, and the product extracted with very dilute hydrochloric acid, a residue of yellow microscopic crystals resembling cubes and octahedra of the composition



and of specific gravity 5.91 remains undissolved. These crystals are found on examination by polarised light to consist of aggregations of rhombic lamellæ.

**Reactions of the compounds of barium.** When heated on a thin platinum wire in the inner blowpipe flame, or when brought into any non-luminous flame, barium compounds impart a yellowish-green colour to the outer flame. When viewed through the spectroscope two green lines  $\text{Ba}\alpha$  and  $\text{Ba}\beta$  come out most intensely;  $\text{Ba}\gamma$ , though not so marked, is also a peculiarly distinct line. Besides these, there are numerous lines in the red and yellow and one broad indistinct line in the blue, close to Fraunhofer's F. Buusen found that  $\frac{1}{1000}$  of a milligram of barium salt may be detected spectroscopically. Silicates of barium give this reaction on moistening with strong hydrochloric acid.

The hydrate, sulphide, chloride, bromide, iodide, nitrate, and many organic salts of barium are soluble in water, and all are poisonous. The majority of the remaining salts are soluble in hydrochloric and nitric acids, while the sulphate and silicofluoride are insoluble in all acids.

Alkaline carbonates precipitate white barium carbonate, soluble in most acids, hence ammonium carbonate is used to precipitate it (along with the carbonates of strontium and calcium) in qualitative analysis.

Potassium and sodium hydrates, free from carbonates and sulphates, give a voluminous precipitate of barium hydrate  $\text{Ba}(\text{OH})_2$ , with concentrated solutions soluble in more water. Ammonia gives no precipitate.

Sulphuric acid, as well as all soluble sulphates, throws down barium sulphate from all solutions of barium salts. Pickering (C. N. 46, 223) states that the smallest quantity of barium which can be detected is 1 part in 833,000 parts of water. The presence of an alkaline citrate greatly interferes with the precipitation. Strontium sulphate (which is more soluble) forms a delicate test for barium.

Phosphate, arsenate, borate, and iodate of sodium also give precipitates soluble in acids.

Ammonium oxalate gives, from moderately dilute solutions, a white pulverulent precipitate of barium oxalate.

Potassium chromate precipitates bright lemon-yellow barium chromate, soluble in nitric, hydrochloric, or chromic acid.

Hydrofluosilicic acid gives a colourless crystalline precipitate of barium silicofluoride; this reaction will detect 1 part of the chloride in 3,800 parts water. The precipitate is nearly insoluble in nitric and hydrochloric acids, more insoluble in alcohol.

Barium is readily distinguished from lead (which also forms a sulphate insoluble in water) by the fact that sulphuretted hydrogen gives a black precipitate of lead sulphide with soluble lead salts.

Soluble barium salts are at once distinguished from those of strontium and calcium by the fact that they are immediately precipitated by a solution of calcium sulphate, which only gives a precipitate with strontium salts on standing. The hydrofluosilicic acid reaction is also of use in separating barium from the other two metals. Barium chloride is also insoluble in alcohol while the chlorides of strontium and calcium are soluble, and the nitrates of barium and strontium are insoluble in alcohol while calcium nitrate is soluble. From these facts a scheme of separation is readily derived, the precipitated carbonates of barium, strontium, and calcium being converted into chlorides, and the chlorides of strontium and calcium dissolved out by alcohol, leaving a residue of chloride of barium. The strontium and calcium may then be separated by converting their reprecipitated carbonates to nitrates and dissolving out the calcium nitrate (*v. ANALYSIS*).

**Estimation of barium.** Barium is generally estimated in the form of sulphate, which is precipitated from the hot solution of the weighed quantity of substance by dilute sulphuric acid, which must be added in considerable excess to prevent the original undecomposed salt from being carried down by the sulphate.

The precipitate is often discoloured by iron, from which it may be freed by boiling the precipitate, after settling and decantation, with 5 to 10 c.c. of hydrochloric acid, neutralising with ammonia and re-acidifying, after which treatment it becomes perfectly white.

In its organic salts barium may be estimated as carbonate by ignition in a platinum crucible and subsequent moistening of the residue with a concentrated solution of ammonium carbonate, evaporation, gentle ignition, and weighing.

Barium may be estimated in presence of strontium, calcium, and magnesium by precipitating it from solutions containing acetic acid as chromate by means of potassium chromate, collecting the precipitate upon a weighed filter, and washing with dilute acetic acid containing potassium chromate, Frerichs (*B.* 1874, 800 and 956), Morse (*A. C. J.* 1880 [2] 176). A. F. T.

**BARK BREAD.** A kind of bread formerly made by the peasants in various parts of Norway from the inner bark of *Pinus sylvestris*.

**BARKLYITE** *v.* CORUNDUM.

**BARLEY** *v.* CEREALS.

**BARUS CAMPHOR** *v.* CAMPHORS.

**BARWOOD** *v.* SANDERSWOOD.

**BARYTA GREEN** *v.* BARIUM.

**BARYTIC WHITE**, or **PERMANENT WHITE**, or **BLANC FIXE** *v.* BARIUM; also PIGMENTS.

**BARYTO-CELESTINE** *v.* STRONTIUM.

**BASIC BESSEMER STEEL** *v.* IRON.

**BASILICON.** A mixture of oil, wax, and resin. Resin cerate.

**BASLE BLUE** *v.* AZINES.

**BASSIA** or **MAHWA FLOWERS.** The flowers of *B. latifolia* or Mahwa, a tree growing to the height of 60 ft., very abundant in Central India, are very succulent and fall from the tree in large quantities every night, a single tree affording from 200 to 400 lbs. of flowers in a season, which lasts during March and April. They are used as an article of food, both cooked and raw. By fermentation and distillation they

yield 6·16 gallons of proof spirit per cwt. It is of a very superior quality, and when the operations have been carefully performed, is very much like good Irish whisky, having a strong smoky and rather fetid flavour, which disappears with age.

They have also been used as a cattle food with success. It is said that the flesh of pigs and other animals is much improved, acquiring a delicate flavour.

Church (*Gard. Chron.* 1886, 86) found 56 p.c. sugar, 3·2 p.c. of which was sucrose, but only 2·2 p.c. of nitrogen; hence these flowers ought to be mixed with nitrogenous foods.

Recently the dried flowers have been recommended as a source of sugar. Negri found in them 57·9 p.c. of glucose yielding 26·74 p.c. of alcohol on distillation (*Rev. Chim. Med. Pharm.* 2, 384).

**BASSIA OILS.** The best known oil is obtained from *Bassia (Butyrospermum) Parkii*, a tree growing in Africa. By boiling its seeds in water, a white bland fat of an agreeable taste is obtained; it is known in commerce as Bambara-, Bambui-, Galam-, or Shee butter. It soon turns yellowish and rancid in hot climates. This tree also yields a gutta-percha, of sp.gr. 0·976, which becomes electrical by friction, is more insoluble in light petroleum oil, of turpentine and hot acetic acid than ordinary gutta-percha, softens in warm water, and can be used for galvanoplastic and insulating purposes (Hackel *u.* Schlagdenhaffen, *C. R.* 101, 1,069; Jackson, *P. J. T.* [3] 8, 646).

From *Bassia butyracea*, known as *Phulwa* or Indian butter tree, a soft white fat can be extracted by bruising and pressing the seeds. This keeps well, makes a good soap, and burns with a bright light, without smoke or smell. The residual cake is used as a food material. The 'Butter of Allipa,' described by Riche *u.* Remont (*J. Ph.* [5] 1, 215) which melts at a higher temperature than other similar bodies, and the use of which is recommended for the manufacture of tapers, is probably this fat and not that derived from *B. longifolia*.

*Bassia longifolia*, *Illipe* or *Ilipe*, is a tree growing to a height of 40 ft., found in the forests of Western Mysore; the oil derived from the seeds retains its solidity at a moderate temperature, but turns rancid quickly if the weather be warm.

From the seeds of *Bassia latifolia* a fluid greenish oil is expressed, which keeps well in cool climates, and is used in the manufacture of soap. Valenta (*D. P. J.* 251, 461) describes the seeds as 1 to 2 cm. long, inclosed in a brown skin, and as possessing a bitter aromatic taste and peculiar odour. The seeds dried at 100°C. contained

Fat (extracted by light petroleum)	51·14
„ soluble in absolute alcohol	7·83
Tannin	2·12
Bitter principle, soluble in water	0·60
Starch	0·07
Vegetable mucilage	1·65
Albuminous substances soluble in water	3·60
Extractive substances soluble in water	15·59
Insoluble proteids	4·40
Total ash	2·71
Fibre and loss	10·29

The fat had a sp.gr. of 0·9175 at 15°, melted at 25°·3, and solidified, at 17°·5 to 18°·5.



The composition of the commercial fats is very variable; they are probably mixtures of oils from different species. Hardwick found in a sample melting between 27° and 30°C. and having a sp.gr. of 0.958, oleic and bassia acids, and glycerol. The sample was sparingly soluble in anhydrous alcohol and ether (C. T. J. 2, 231). O. Henry found stearine to predominate; Pelouze a. Bourdet olein; Buff could not detect palmitic acid. Thomsen a. Wood discovered an acid melting at 70° identical with stearic acid.

According to Schädler the *Bassia longifolia* fat consists of 80 p.e. stearin and 20 p.e. olein, whilst Valenta finds 63.49 p.e. oleic acid and 36.51 p.e. of a fatty acid melting at 62°, essentially the same as palmitic acid, and Max Buchner (C. C. 15, 257) found 80 p.e. of palmitic acid melting at 60°.

For a further account v. Jackson (P. J. T. [3] 8, 646).

#### BASSORA GUM v. GEMS.

**BATATA, or SWEET POTATO**, the tuber of *Batata edulis*, a plant belonging to the convolvulus family, cultivated in warm climates.

According to Savallé it is an excellent source of alcohol, 100 kilos. of tubers yielding from 12 to 13 litres of 100 p.e. alcohol. The tubers contain 10.20 p.e. of sugar and 16.05 p.e. of starch (Ralu, Reinke), v. Am. S. [3] 13, 197, 202; C. N. 40, 195; Savallé, W. J. 32, 120; Ralu, Rev. Univers. Distillerie, 1885, 593; Reinke, Zeitschr. f. Spiritus Industrie, 1885, 375.

**BATH BRICK.** A brick made from deposits of siliceous and calcareous earth at Bridgewater, Highbridge, and elsewhere, and used for polishing metals.

**BATH-METAL.** An alloy of copper and zinc containing a larger proportion of copper than ordinary brass, viz. 83 p.e. copper to 17 p.e. zinc, sp.gr. 8.451; fracture crystalline, and colour yellowish-red.

#### BAUXITE v. ALUMINIUM.

#### BAY-SALT v. SODIUM CHLORIDE.

#### BDELLIUM v. GUM RESINS.

**BEBEERU BARK.** The dried bark of *Nectandra Rodiei*, the greenheart tree, obtained from British Guiana, contains beberine, to which its strong persistent bitter taste is due. Occasionally used as a tonic and antiperiodic.

**BEECH NUT OIL.** A clear light yellow, viscid, inodorous oil, of sp.gr. 0.9225 at 15°, obtained by subjecting beech nuts to pressure. Coloured rose-red by nitric acid. It is non-drying, makes a good white soap, and is used in cooking and as a lamp oil (Lefort, C. R. 35, 734).

According to Boehm (Ar. Ph. [3] 22, 159) the cake contains an organic base termed lurido-cholin.

**BEECH TAR.** According to Fisher, 100 parts of beech wood yield on dry distillation 45 parts of acetic acid, 23 parts of charcoal, 4 of oil, and 28 of gas, consisting of 20 parts carbonic dioxide, 7 of carbon monoxide, 0.5 of marsh gas, 0.05 of hydrogen, and 0.15 of water (D. P. J. 238, 55).

The tar contains phenol, cresol, phlorol, guaiacol, and cresol, the dimethyl ether of propyl pyrogallol, the dimethyl ether of pyrogallol, which on oxidation yield cærulignone or cæliret, pittacal, and picamar.

According to Gratzel (J. Ph. [5] 6, 520) ferric chloride colours beech tar creosote a blue passing to brown.

For a history of the investigations made upon wood tars v. Schorlemmer (S. C. I. 4, 152), where also will be found a bibliography of the subject (v. also CREOSOTE, and WOOD, DESTRUCTIVE DISTILLATION OF).

**BEEGERITE.** A sulphide of bismuth and antimony found in Park Co., Colorado.

	a	b
S . . . .	11.97	16.39
Bi . . . .	20.59	19.35
Pb . . . .	64.23	45.37
Cu . . . .	1.70	1.12
Ag . . . .	—	9.98
Fe . . . .	—	2.89
Insol. . . .	—	0.12
Total . . . .	101.49	95.72
Sp.gr. . . .	7.273	6.565

(a) König, A. C. J. 2, 379.

(b) König, Z. K. 11, 290.

#### BEER v. BREWING.

**BEESWAX.** Wax is really secreted by bees, and not collected from plants. If bees are fed with pure sugar or honey they will continue to produce wax (A. 162, 235; C. J. 25, 639). Beeswax melts at 64°–65°, sp.gr. 0.96931; sometimes found adulterated with Japanese wax, which is cheaper, but is heavier and of lower melting-point. A table of sp.gr., melting and solidifying points of mixture of pure beeswax and Japan wax, is given C. R. 78, 1,544, abs. C. S. J. 27, 1,026. Wax is often adulterated with tallow. Pure wax floats on alcohol of 29°. By observing the strength of alcohol on which a sample floats, the percentage of pure wax may be deduced.

If alcoholometers shows 29.0 = 100 p.e. pure wax

"	"	39.63 = 75	"	"
"	"	50.25 = 50	"	"
"	"	60.87 = 25	"	"
"	"	71.50 = 0	"	"

(Hardy, C. C. 1872, 538; C. J. 26, 655.)

Adulteration with eerosin is detected by boiling with strong alcoholic potash and keeping the mixture warm and at rest for some time; if the wax is pure the solution remains clear; if eerosin be present paraffin will float to the top (D. P. J. 231, 272; C. J. 1879 [2] 675).

Adulteration with resin may be detected in the following way: 5 grams of the wax are boiled for one minute with 25 grams nitric acid (1.33 sp.gr.), the liquid somewhat diluted and saturated with ammonia; if the wax is pure the alkaline liquid is yellow, if resin was present the liquid has a dark-brown colour. 1 p.e. of resin can be detected in this way (A. Ph. [3] 13, 212; abs. C. J. 1879 [2] 283).

If the sp.gr. of wax is higher than 0.961, adulteration with stearin, resin, or Japan wax may be suspected; if lower than 0.956, paraffin, ozokerit, or tallow is probably present (D. P. J. 238, 356; abs. C. J. 1881 [2] 316).

For tables of sp.gr. of wax and of substances used in adulterating it, see Arch. Pharm. [3] 20, 454; abs. C. J. 1882 [2] 1,139.

Method of testing beeswax for adulterations with other waxes by estimating the ratio of the total alkalis (KOH) required for complete saponification to that required to neutralise the free

acid is given in D. P. J. 249, 338; abs. C. J. 1884 [2] 506.

Tables of analyses of waxes from many different places average 14.4 p.c. cerotic acid and 88.09 myricin (D. P. J. 251, 168; abs. C. J. 1884 [2] 779).

If yellow wax is exposed in thin shreds to air and sunlight it is slowly bleached and becomes somewhat less fusible. It can also be bleached by nitric acid. Chlorine bleaches, but also combines with it. If boiled with nitric acid it is readily oxidised, being converted into an oil containing pimelic, adipic, and lipoic acids. By long heating succinic acid is produced. Wax is soluble in sulphuric acid at 60°C.; at a higher temperature it is carbonised.

By boiling with alcohol it may be separated into three substances: (1) myricine or myricic palmitate  $C_{18}H_{34}(C_{26}H_{52})O_2$ , insoluble in boiling alcohol; (2) cerotic acid  $C_{22}H_{42}O_2$  crystallising from boiling alcohol; (3) cerolein, which remains dissolved in cold alcohol. Beeswax is decomposed on distillation, giving off  $CO_2$  and  $C_2H_4$ , acetic and propionic acids, a white thick oil or 'wax butter,' and a carbonaceous residue. On distilling with lime nearly the same products are obtained.

Wax is very slowly saponified by boiling with potash solution, but if the wax is melted and mixed with fused potash, a little gas is given off, and the whole is very readily converted into a thick amber-coloured soapy mass, soluble in a large quantity of boiling water, and precipitated from solution by addition of salt. On addition of hydrochloric acid to the solution a white waxy neutral substance separates (C. J. 1, 248).

Beeswax is partially soluble in alcohol, and ether, and completely soluble in chloroform. The soap formed by boiling with alcoholic potash is difficultly soluble in hot water. By these characteristics it may be distinguished from other waxes (Ph. [3] 10, 749; abs. C. J. 1880 [2] 763).

The non-acid part of beeswax contains a mixture of hydrocarbons and alcohols. Among the hydrocarbons are  $C_{22}H_{42}$  and  $C_{31}H_{64}$ ; among the alcohols are myricyl  $C_{31}H_{64}O$  and ceryl  $C_{29}H_{58}O$ , also  $C_{27}H_{54}O$  and  $C_{24}H_{48}O$  (?) (A. 235, 106; abs. C. J. 1887 [2] 124) (v. WAX).

**BEET-ROOT.** (Fr. *Betterave*; Ger. *rothe Rübe*.) The root of the beet. Two distinct species of the genus *Beta* are cultivated. *B. hortensis* is grown for its succulent leaves; *B. vulgaris* for its long fleshy root. The red variety of *B. vulgaris* is used as a vegetable, whilst the white variety is extensively cultivated as a source of sugar (v. SUGAR).

**BEET-ROOT GUM** v. GUMS.

**BEHENIC ACID** v. FATTY ACIDS.

**BELLADONNA.** (Fr. *Belledame*.) The *Atropa Belladonna*, or deadly nightshade. A poisonous plant of the *Solanaceæ* order. Employed in medicine as an anodyne &c., and for dilating the pupil. The name appears to have been derived from the circumstance of its employment in an Italian cosmetic. Its physiological action is due to *atropine* (v. VEGETO-ALKALOIDS).

**BELL-METAL.** An alloy of copper and tin used in the manufacture of bells. Contains from 3 to 4 parts of copper to 1 part of tin.

**BELLITE.** An explosive prepared by mixing a nitrate with a nitro-compound such as dinitro-

benzene, trinitronaphthalene, or nitrotoluene, and then subjecting the mixture to a temperature of from 50° to 100°C. (Eng. Pat. 13,690, Nov. 10, 1885; v. EXPLOSIVES).

**BELL-METAL ORE.** A sulphide of copper, tin, and iron, with more or less zinc, occasionally met with in the Cornish mines. Known also as *stannine*. Composition: (a) From Huel Rock, by Kudsneath, (b) from Zinnwald, by Rammelsberg, (c) from St. Michael's Mount, by Johnston:

	Cu	Fe	Zn	Pb	Sr	S
(a)	29.69	12.57	1.79	—	25.81	29.95 = 99.81
(b)	26.31	6.80	6.93	0.41	23.94	29.89 = 99.28
(c)	23.55	4.79	10.11	—	31.62	29.93 = 100.00

**BEN, OIL OF.** A fatty oil expressed from the decorticated nuts of *Moringa Nux Behen*. It is nearly colourless and odourless, and does not readily oxidise or become rancid. Formerly used in perfumery to abstract the odorous principles of plants and as an embrocation for rheumatism. Contains in addition to oleic and margaric acids two fatty acids—*benomargaric acid*  $C_{15}H_{30}O_2$  (Walter, C. R. 22, 1,143) m.p. 52°, and *benostearic acid* or *behenic acid*  $C_{22}H_{44}O_2$  (Stricke, A. 64, 346), m.p. 76°. Behenic acid is found also in the oil from black mustard seed (Goldschmidt).

**BENGAL LIGHTS.** These fires may be made by mixing potassium chlorate, carbon, antimony sulphide, strontium nitrate, &c., together in suitable proportions, but all such mixtures of potassium chlorate and sulphur are dangerous from their tendency to inflame spontaneously owing to sulphur frequently containing sulphuric acid. Clouet (J. Ph. [5] 4, 458) has found from 0.30 to 2.187 grams of sulphuric acid in the kilogram of sulphur; he recommends that it should be washed. Saunders suggests that 120 grains of potassium bicarbonate should be added to each pound of sulphur to neutralise the free acid.

A list of coloured fires of various speeds in burning will be found in Cooley's Encyclopædia, 1, 738.

An improvement in the manufacture of Bengal lights has been suggested by Chertier (W. J. 24, 464), who obtains a smokeless and odourless fire by melting shellac and adding with continuous stirring the nitrate. The proportions given are, for red fires, one part of shellac to five of strontium nitrate; for green, one of shellac to five of barium nitrate; and for yellow, one shellac to three sodium nitrate. They burn slowly and are well adapted for theatres &c.

C. Schmidt has patented (Ger. Pat. 34,020, 1885) the following process. From one to ten grams of magnesium dust are added to 100 grams of collodion, and three grams of barium or strontium chloride are added. On evaporation of the ether, thin plates are obtained which burn with great brilliancy.

Another formula recommended by a German firm is, for white fires, to fuse one part shellac with six barium nitrate, grind and mix with 2.5 parts magnesium powder. For red fires five parts strontium nitrate is used instead of the barium nitrate. These mixtures can be made into ribbons or charged into thin zinc tubes so as to make torches (D. P. J. 256, 518).

**BENGALIN** v. INDULIN.

**BENJAMIN, GUM,** v. BALSAMS.

**BENZAL CHLORIDE.** *Benzylidene chloride*, *Benzidene chloride*, *v.* **TOLUENE**, **CHLORINE DERIVATIVES OF**.

**BENZALDEHYDE**  $C_6H_5O = C_6H_5 \cdot CHO$ . *Benzzoic aldehyde*, *Benzoyl hydride*. *Ethereal*, or *volatile*, or *essential oil of bitter almonds*. *Essence of bitter almonds*. (*Aldehyde benzoïque*, Fr.; *Benzaldehyd*, Ger.) Mortrès showed, in 1803, that, in addition to the fatty oil, a volatile oil could be obtained from bitter almonds; but pure benzaldehyde was first isolated, its composition determined, and its reactions studied, by Liebig and Wöhler in 1837 (A. 22, 1). Benzaldehyde is not contained, as such, in bitter almonds: it is produced by the action of a soluble ferment, *emulsin* (also termed *synaptase*), present in the almond, on *amygdalin*  $C_{20}H_{27}NO_{11}$ . In this fermentation, which occurs when the bruised almonds are mixed with cold water, the amygdalin is hydrolysed, yielding benzaldehyde, together with hydrocyanic acid and glucose:

$C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5O + HCN + 2C_6H_{12}O_6$ .  
If boiling water is used, the ferment is destroyed and the reaction does not take place. Peach kernels and other kernels of stone fruits containing amygdalin also yield benzaldehyde. It occurs, ready formed, in the leaves of the cherry laurel (*Prunus laurocerasus*), of the bird cherry (*Prunus Padus*), and of the peach (*Amygdalus persica*).

*Preparation*.—1. *From bitter almonds*. The bitter almonds (or more rarely, peach kernels) are ground and then cold-pressed, to extract the fatty oil. The press-cake is made into a thin cream with cold water, introduced into a still, allowed to stand for 24 hours, and then distilled either by blowing in superheated steam, or, less advantageously, over a fire, in which case mechanical stirring must be employed to prevent the charring of the vegetable matter. The distillation is continued as long as the distillate appears milky. Most of the crude benzaldehyde separates as an oily layer under the aqueous distillate; some, however, remains in solution and may be recovered by distilling the aqueous liquid, when the benzaldehyde passes over with the earlier portions.

Michael Pettenkofer (A. 122, 77) modifies the foregoing process as follows:—12 parts of the coarsely powdered press-cake are added to 100–120 parts of boiling water, stirring during the process, and the mixture is kept boiling for about half an hour. In this way all the amygdalin is obtained in solution. The liquid is then allowed to cool; 1 part of ground bitter almonds, suspended in 6–7 parts of cold water, is added, and after standing for 12 hours the whole is slowly distilled. According to Pettenkofer, the maximum yield of benzaldehyde is thus obtained, no amygdalin remaining undecomposed. Pelz, however, states (J. 1864, 654) that the yield of benzaldehyde in this process is no greater than is obtained by macerating merely the above-mentioned 1 part of ground bitter almonds with cold water and then distilling.

The oil prepared by either of these methods contains hydrocyanic acid, from which it may be freed by fractional distillation, the hydrocyanic acid coming over with the first part of the distillate. The hydrocyanic acid may also be removed without distillation by shaking the

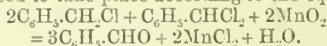
oil with a mixture of milk of lime and ferrous sulphate (Liebig and Wöhler). The purest benzaldehyde is obtained by shaking the crude product with 3–4 times its volume of a concentrated solution of sodium bisulphite, washing the crystals of the double compound

$(C_6H_5O, NaHSO_3) \cdot H_2O$   
with alcohol, recrystallising them from water and distilling them with a solution of sodium carbonate (Bertagnini, A. 85, 183; Müller and Limpriht, A. 111, 136).

2. *From toluene*. At the present day benzaldehyde is generally prepared artificially from chlorinated derivatives of toluene. The following are the chief processes that have been proposed:

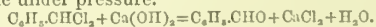
Lauth and Grimaux (Bl. [2] 7, 105) boil 1 part of benzyl chloride  $C_6H_5 \cdot CH_2Cl$ ,  $1\frac{1}{2}$  parts of lead nitrate (or copper nitrate), and 10 parts of water with a reflux condenser for several hours, passing a current of carbon dioxide through the apparatus to prevent oxidation. Half the liquid is then distilled off, and the oil, which separates in the distillate, is rectified. The product, which consists mainly of benzaldehyde, may be further purified by converting it into the bisulphite compound.

H. Schmidt (G. P. 20,909; S. C. I. 1883, 274) chlorinates boiling toluene until it attains a sp.gr. of 1.175, when it consists essentially of a mixture of 2 mols. of benzyl chloride with 1 mol. of benzal chloride. This product is boiled with six times its volume of water and a quantity of powdered black oxide of manganese containing two atoms of available oxygen to the above molecular proportion. The reaction is supposed to take place according to the equation



The product is steam-distilled, and the aldehyde purified in the usual way. A mixture of benzyl bromide and benzal bromide may be substituted for the chlorine compounds.

Another method now generally employed consists in heating benzal chloride with milk of lime under pressure.



According to Espenschied (G. P. 47,187) the reaction takes place under ordinary pressures if insoluble substances such as chalk or barium sulphate are added along with the milk of lime, so as to produce an emulsion of the benzal chloride.

E. Jacobsen (G. P. 11,494 and 13,127; B. 13, 2,013, and 14, 1,425) heats benzal chloride with an organic acid (or an ethereal salt of an organic acid) and a metallic chloride, oxide, or sulphide. Thus benzal chloride, when heated on the water-bath with acetic acid and a little zinc chloride, yields benzaldehyde, acetyl chloride, and hydrochloric acid

$C_6H_5 \cdot CHCl_2 + CH_3 \cdot CO_2H = C_6H_5 \cdot CHO + CH_3 \cdot COCl + HCl$ .  
The acetyl chloride, owing to its much lower boiling-point, may be readily removed from the benzaldehyde by distillation.

*Other modes of formation*.—Benzaldehyde is also formed in the following reactions, which, however, are not of practical importance. By distilling a mixture of calcium benzoate and calcium formate (Piria, A. 100, 105); by the oxidation of benzyl alcohol (Cannizzaro, A. Ch. [3]

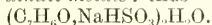


40, 234), or of cinnamic acid (Dumas and Peligot, A. 14, 50); by the reduction of benzoic acid, either with sodium amalgam in acid solution (Kolbe, A. 118, 122), or by passing its vapour over heated zinc-dust (Baeyer, A. 140, 296); by treating toluene with chromyl chloride and then with water (Étard, A. Ch. [5] 22, 225).

**Properties.**—Benzaldehyde is a colourless, strongly refractive liquid with a pleasant aromatic odour, boiling at 179–180°. Sp.gr. 1.0504<sup>15</sup> (Mendelëff, J. 1860, 7). It is soluble in 300 parts of water, and miscible in all proportions with alcohol and ether. It is non-poisonous, the poisonous properties of ordinary oil of bitter almonds being due to the presence of hydrocyanic acid.

**Reactions.**—Benzaldehyde readily undergoes oxidation: thus it absorbs oxygen from the air, forming benzoic acid. The presence of hydrocyanic acid protects it from oxidation; according to Dusart (Bl. 8, 459), it is therefore usual to add hydrocyanic acid to artificial benzaldehyde. Taken internally, benzaldehyde is oxidised in the organism, reappearing in the urine as hippuric acid. Aqueous caustic potash converts it into benzoic acid and benzyl alcohol

$2C_6H_5CHO + KOH = C_6H_5CO_2K + C_6H_5CH_2OH$ .  
It forms crystalline compounds with the bisulphites of the alkali metals: thus



Under the influence of dehydrating agents it readily undergoes condensation with various other substances: thus when heated with acetic anhydride and dry sodium acetate it yields cinnamic acid

$C_6H_5CHO + CH_3CO_2H = C_6H_5CH : CH.CO_2H + H_2O$   
(Perkin, C. J. 31, 389), and with dimethylaniline in presence of zinc chloride it forms the compound  $C_6H_5CH(C_6H_5.NMe_2)_2$ , the leuco-base of benzaldehyde green, which by oxidation is converted into that colouring matter (O. Fischer, B. 11, 950).

**Uses.**—Benzaldehyde is employed in the manufacture of benzaldehyde green and similar colouring matters. Formerly artificial cinnamic acid was prepared from it, but is now obtained direct from benzal chloride. Essence of bitter almonds is used as a flavouring ingredient by cooks and confectioners, and also in perfumery.

**Impurities and adulterations.**—Benzaldehyde very frequently contains hydrocyanic acid, either originally present or subsequently added (*v. supra*), and benzoic acid, formed by spontaneous oxidation. The artificial product generally contains chlorinated benzaldehydes. Alcohol, ethereal oils, and nitrobenzene are sometimes fraudulently added; the latter substance resembles benzaldehyde in smell.

In order to test the purity of a sample of benzaldehyde the sp.gr. and boiling-point should first be determined, as both of these are altered by the presence of impurities. The substance should also dissolve without residue in a solution of sodium bisulphite.

Of the impurities above mentioned, hydrocyanic acid may be detected by distilling the oil and then testing the first portions of the distillate by the Prussian-blue test; chlorine compounds, by heating the oil with metallic sodium, when sodium chloride will be formed, in which the chlorine can be detected by silver

nitrate, taking care, however, to distinguish between silver chloride and silver cyanide, as this latter will be formed if hydrocyanic acid or nitrobenzene is present; alcohol, by the iodoform test; and ethereal oils or nitrobenzene, by dissolving the sample in sodium bisulphite, when these admixtures remain behind. Bourgoin (B. 5, 293) tests for nitrobenzene in benzaldehyde by mixing the sample with twice its volume of caustic potash: if nitrobenzene is present the mixture turns green, and on adding water the liquid forms two layers, of which the under layer is yellow and the upper green, this latter turning red on standing for some hours.

**Substitution derivatives of benzaldehyde.**

None of the substitution derivatives of benzaldehyde are of technical importance. *Orthonitrobenzaldehyde*  $C_6H_4(NO_2)CHO$  (1, 2) is of interest, since it yields indigotin when treated with acetone and caustic soda (Baeyer, B. 15, 2,856). The discovery of a process by which orthonitrobenzaldehyde could be readily obtained from orthonitrotoluene would bring the problem of the economical production of artificial indigo considerably nearer to solution. Unfortunately, the reactions by which toluene is converted into benzaldehyde fail when applied to orthonitrotoluene, and at present orthonitrobenzaldehyde is prepared by the costly process of oxidising orthonitrocinnamic acid.

Processes for preparing chlor- and brombenzaldehydes have been patented. These compounds may be used in the preparation of chlorinated or brominated benzaldehyde greens; or the nitro-group may be readily introduced in the ortho-position to the aldehyde group, and the resulting halogenitrobenzaldehydes converted by treatment with acetone and caustic soda into chlorinated or brominated indigotins. None of these colouring matters are manufactured.

F. R. J.

**BENZALDEHYDE GREEN v. TRIPHENYLMETHANE COLOURING MATTERS.**

**BENZAURINE v. AURINE.**

**BENZENE AND ITS HOMOLOGUES.**

**Benzene.** (*Benzol*, *Benzole*, Fr.; *Benzol*, Ger.)

The name of this substance was derived in its original form from that of gum benzoin, probably as *benzoïn olerum*, hence *benzole*, which latter form is still in use amongst nearly all distillers and users of it both in this country and on the Continent. In more strictly scientific literature, however, the name *benzene* has now become generally accepted, and the systematic termination *ene* is employed in the names of its various homologues, as toluene, xylene, cymene, &c.

Pure benzene is a limpid, colourless, highly refracting liquid at ordinary temperatures. Its sp.gr. at 0° is 0.8991 (Kopp), 0.90023 (Adrienz), and at 15° 0.8841 (Mendelëff).

Its refraction index for the D line at 15°·2 is 1.4957 (Adrienz), at 9° 1.4593 for A, 1.5050 for D, 1.5037 for H (Gladstone).

When surrounded by ice it becomes solid, and if crystallisation is allowed to take place slowly, rhombic crystals are produced, whose axes *a*, *b*, *c*, are 0.891, 1, 0.799 (Groth). The solid melts at 4.45 (Regnault), at 5.5 according to Mansfield, at 7° according to Mitscherlich, who used that from natural benzoic acid.

Faraday found that it expands  $\frac{1}{10}$  of its bulk on solidification, which, though the melting-point is so high, never seems to occur above  $0^{\circ}$ .

It exhibits no absorption lines or bands in the visible portion of the spectrum. Beyond H, however, photographs show a series of four bands covering the region lying between W. L. 3,171 and 2,190 tenth-metres. The methylated benzenes, toluene, and the three xylenes exhibit a very similar absorption, requiring indeed very careful measurement to distinguish one from the other (Hartley, C. S. J. 47, 685).

Benzene is an excellent solvent, easily dissolving caoutchouc and asphaltum, if they have not been exposed to light, though the protective effect of the light on the asphaltum is but slight, and prolonged treatment with benzene causes it to dissolve. Nearly all the gum resins, sulphur, phosphorus, fats, oils, most of the natural alkaloids, and many other organic compounds are soluble in it. It has also, in common with carbon disulphide, the property of dissolving iodine with production of a violet solution.

Benzene is itself soluble to a very slight extent in water, considerably more so in alcohol, whilst ether, glacial acetic acid, and carbon bisulphide, dissolve it readily. It also dissolves in concentrated sulphuric acid, producing a crystalline molecular compound corresponding to one of the hydrates, but extremely unstable. Certain compounds are known which crystallise with benzene in definite molecular proportions.

Benzene boils under normal pressure at  $80.36^{\circ}$  (Regnault). For benzene from coal-tar Adrieenz found  $80.53$  to  $80.62$ ; and for that obtained from benzoic acid prepared from gum benzoin,  $80.60$  to  $80.67$ .

The vapour when inhaled produces giddiness and ultimately insensibility.

Benzene forms with picric acid the molecular compound  $C_6H_4(NO_2)_3OH \cdot C_6H_6$  which melts with decomposition at  $90^{\circ}$ .

Oxidising agents, such as potassium permanganate or manganese dioxide and sulphuric acid convert it into formic, propionic, and oxalic acids together with small quantities of benzoic and phthalic acids, the latter substances being produced by the simultaneous oxidation of formic acid and benzene, the process of condensation resembling that occurring in the conversion of dimethylaniline into methyl violet. When strongly heated in sealed tubes or when passed slowly through strongly heated open tubes, condensation and decomposition go on together, acetylene, diphenyl, diphenylbenzene, &c., being formed with evolution of hydrogen and deposition of carbon.

There can be little doubt that toluene and xylenes can also be produced in this way, and since Berthelot has shown that toluene and xylene when passed through strongly heated tubes can produce anthracene and naphthalene, and since he also obtained anthracene by so treating a mixture of benzene and ethylene, we may assume that if benzene is *not* the mother substance of the whole series of hydrocarbons obtained from coal tar, it is yet capable under proper conditions of generating all the others.

When chlorine acts upon pure benzene in sunshine, benzene hexachloride  $C_6H_2Cl_6$  is formed. Impure benzene is said not to undergo

this change. The substitution of chlorine for hydrogen in the nucleus or benzene ring is a very slow operation if chlorine alone is used, but if in every litre of benzene about 10 grams of iodine are dissolved and the liquid kept boiling while a brisk current of chlorine is passed into it, substitution readily takes place and chlorinated benzenes are produced. The reaction may be continued until the whole of the hydrogen is replaced with production of hexachlorobenzene  $C_6Cl_6$ . From the nature of the reaction it need scarcely be pointed out that there is no possibility of obtaining exact replacements, and that until the whole of the hydrogen has gone, a mixture of benzene and chlorinated benzenes is present. Corresponding bromino and iodine compounds, and at least one fluorine compound, are known.

When subjected to the action of strong nitric acid or a mixture of nitric and sulphuric acids, substitution of hydrogen by  $NO_2$  takes place with great ease. If the mixture is kept cool only mononitrobenzene is formed, but if heated, the three dinitrobenzenes are produced, the metadinitro-product (m.p.  $89^{\circ}$ ) always greatly predominating. The ortho- and para-compounds can only be produced in quantity by indirect methods. Trinitrobenzenes can only be obtained by the action of a great excess of a mixture of nitric acid and fuming sulphuric acid.

All the nitro-compounds on reduction with appropriate reagents, such as iron, zinc, or tin, in the presence of acid, preferably hydrochloric and water, yield amido-compounds corresponding with the nitro-compound reduced. Such are aniline  $C_6H_5NH_2$ , the three diamido-benzenes or phenylene-diamines  $C_6H_3NH_2NH_2$  &c.

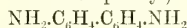
The amido-compounds are by the action of nitrous acid or nitrites in the presence of an excess of acid, preferably hydrochloric, converted into diazo-compounds. If diazobenzene  $C_6H_5N:NCl_2$  be dissolved in absolute alcohol, a current of dry hydrochloric acid passed through the solution and the whole heated, the nitrogen is evolved as gas whilst benzene is regenerated. If a diazo-salt is dissolved in water and boiled in the presence of an acid, nitrogen is also evolved and the corresponding phenol is produced.

The diazo-compounds react with salts of amido-compounds or of phenols in which there is a free para-position, thus generating the almost innumerable series of colouring matters known as azo-dyes (p. page 231). Solutions cooled with ice should be employed, and all rise of temperature must be carefully avoided. Under proper conditions some diazo-compounds, however, attack the amido-group of amido-compounds, forming diazoamido-compounds such as diazoamido-benzene  $C_6H_4N:N \cdot N \cdot C_6H_5$ . These can be made to undergo an isomeric change resulting in the formation of what are known as amidoazo-compounds, of which amidoazobenzene  $C_6H_5N:N \cdot C_6H_5NH_2$  is a typical example. Such bodies, when treated with a reducing agent, split up into an amine- and a paradiamine, while diazo-compounds yield hydrazines only, and diazoamido-compounds a mixture of a hydrazine and an amine.

If the nitro-compounds are submitted to the action of alkaline reducing agents in alcoholic

solution, such as a mixture of zinc-dust and alcoholic soda, the reaction takes a different course altogether. The action of alcoholic soda and heat alone will convert mononitrobenzene into azoxybenzene  $C_6H_5.N=N.C_6H_5$ ; this, by

nascent hydrogen, is converted into azobenzene  $C_6H_5.N=N.C_6H_5$ , which under the action of the same reagent is still further reduced to hydro-azobenzene  $C_6H_5.NH.NH.C_6H_5$ . The latter, when boiled with an acid, is converted into a salt of benzidine (paradiamidodiphenyl)



which is a strongly basic compound isomeric with hydrazobenzene.

When heated with concentrated sulphuric acid or treated in the cold with solutions of  $SO_3$  in  $H_2SO_4$  sulphonic acids are produced by substitution of  $HSO_3$  for hydrogen. These are either mono-, di-, or poly-sulphonic acids, according to the treatment adopted. They are all powerful acids, and form well-defined and generally well-crystallised salts with sodium, potassium, and ammonium, and equally definite, though less easily crystallised salts with calcium, barium, copper, iron, &c. These, especially the sodium or potassium salts, if fused with caustic potash or soda, or heated under great pressure (40 atmospheres) with aqueous soda or potash, are decomposed with production of a sulphite of the alkali metal, and conversion of the benzene residue into the corresponding hydroxy- or phenolic compound.

Only the methyl-homologues of benzene will be considered here, as these alone occur in coal-tar.

The mono-methyl derivative is known as *toluene*, and under all treatments behaves as a completely homogeneous substance.

The di-methyl-derivative is known as *xylene*, the substance of that name occurring in coal-tar, and can be readily split up into three different isomeric compounds: *Orthoxylene* boiling at  $141^\circ$ – $142^\circ$ , which when gently oxidised with weak nitric acid gives a toluic acid melting at  $102^\circ$ ; *Metaxylene* boiling at  $139^\circ$ , which gives a toluic acid melting at  $106^\circ$ ; *Paraxylene* melting at  $15^\circ$  and boiling at  $138^\circ$ , giving a toluic acid melting at  $178^\circ$ .

Each of these different xylenes is, however, absolutely identical in percentage composition, and this isomerism is considered to be due to the *configuration* of the molecule, or in other words to the positions in space occupied relatively to each other, and to the benzene residue, by the two substituting molecules.

This method of regarding the constitution of benzene and its innumerable series of derivatives is usually, for purposes of discussion, investigation, or explanation, represented by drawing a hexagon to represent the molecule of



benzene, the six angles representing the six groups of CH at any of which substitution is supposed to take place. Since only one mono-substitution compound of a given kind (*i.e.* containing a given substituting group) is known, all the six CH-groups in benzene are supposed to be

of equal value. The fact that disubstitution compounds exist in three distinct isomeric modifications (compare the above-mentioned xylenes) is explained in this scheme by the following suppositions as to the relative positions occupied by the substituting groups. First, substitution is supposed to take place at two adjacent angles, *e.g.* 1 and 2, 2 and 3, 4 and 5, &c., in which case the word *ortho* is prefixed to the name of the substance, as orthodimethyl-benzene (commonly called orthoxylene), or orthodichlor-, orthodibrom-, or orthodiamido-benzene, &c. Or the substitution is supposed to take place at two angles not adjacent, but with one interposing, as at 1 and 3, 2 and 4, or 1 and 5, &c. In this case the product is indicated by the prefix *meta*-, as metadimethylbenzene (commonly called metaxylene) &c. Lastly, the substitution is supposed to take place at opposite angles, such as 1 and 4, 2 and 5, 3 and 6, &c. In such a case the substance is known as a *para*-compound, as paradiethylbenzene, or paraxylene, paradininitrobenzene, &c.

This device is due to Kekulé, and satisfactorily agrees with most of the phenomena.

Latterly, to cover certain cases which could not be readily brought into line with it, attempts to introduce an improved formula have been made by Ladenburg, Van 't Hoff, and Le Bel and others, with more or less success.

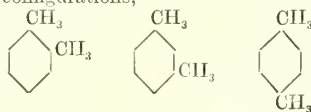
Toluene and xylene generally react under similar conditions in the same way as benzene, producing a similar series of compounds. Since, however, toluene itself is a mono-substituted benzene, mono-substituted toluenes are, *quâ* benzene, di-derivatives. For instance, there is but one mononitrobenzene, but there are three mononitrotoluenes. There are three dinitro- and three diamidobenzenes, but there are six dinitrotoluenes and six diamidotoluenes, and so on.

It is to be borne in mind that in all substitution derivatives higher than the di-substitution series, the number of possible modifications is greater when the substituting groups are dissimilar than when they are all alike: thus, although there are only three isomeric tri-substitution compounds of the formula  $C_6H_3X_3$  or  $C_6H_3Y_3$ , there are six such compounds of the formula  $C_6H_3X_2Y$ .

It follows that the xylenes being di-derivatives, their mono- are, *quâ* benzene, tri-derivatives, and consequently correspond in number with the di-derivatives of toluene.

The introduction of the methyl group, moreover, permits of another kind of substitution which gives rise to a totally different class of bodies from those described above as configurational isomers, in which substitution takes place not in the benzene nucleus, but in the methyl group itself. Such substitution is said to be *extra-nuclear*.

Thus, as mentioned above, there are three substances having the formula  $C_8H_{10}$  known as *ortho*-, *meta*-, or *para*-xylene. These isomers are represented as dimethylbenzenes of the following configurations,





but there is another  $C_6H_{10}$  only known to occur in one form, and always behaving as a mono-derivative of benzene; this is ethylbenzene.



Just as in this case a methyl group has been introduced into the methyl instead of into the nucleus, so chlorine, bromine, &c., may be introduced, and in this manner such bodies as benzyl chloride  $C_6H_5CH_2Cl$ , the di- or tri-chloride, benzaldehyde, and many others are formed.

The physical properties of toluene greatly resemble those of benzene. As solvents, there is little or no difference in their powers, and though the boiling-point of toluene is so much higher than that of benzene, yet in a current of air at ordinary temperatures it evaporates nearly as quickly.

Toluene is a colourless limpid liquid which shows no signs of solidification at temperatures as low as  $-20^\circ$ . Its specific gravity is less than that of benzene, being at  $0^\circ$  0.882, at  $15^\circ$  0.872, its index of refraction at  $25.5$  is for A 1.4709, D 1.4794, H 1.5090 (Gladstone and Dale).

Toluene boils constantly at  $111^\circ$ ; the vapour has much the same physiological effects as that of benzene, but its odour is decidedly less pleasant. If ingested into the stomach, it is eliminated in the urine as hippuric acid.

Of the three xylenes only the meta- has hitherto proved useful in commerce. Orthoxylene boils at  $141.2^\circ$ . Metaxylene boils at  $139^\circ$ , and its specific gravity is 0.8668 at  $19^\circ$ . Paraxylene boils at  $138^\circ$ , and at  $19^\circ$  its gravity is 0.8621. The two former are liquid at all temperatures down to at least  $-20^\circ$ , but paraxylene becomes solid when exposed to a freezing mixture, and when once frozen it only melts at  $15^\circ$ .

The xylenes are distinctly less volatile than toluene and benzene in an air current. The smell of the vapours is unpleasant and pungent, and they possess the power of producing unconsciousness when inhaled.

Both benzene and toluene when prepared from coal tar are accompanied by sulphur compounds known as thiophenes. That derived from benzene, no doubt by the action of sulphur from the pyrites of coal at a high temperature during distillation in the gas-retort, is represented by



It was isolated in 1882 by V. Meyer, who obtained by constant and repeated agitation with sulphuric acid about 2 kilos. from 2,000 kilos. of commercial benzene. It is a colourless liquid, boiling constantly at  $84^\circ$ ; specific gravity at  $15^\circ$  1.100. In many of its reactions it behaves exactly like benzene.

Thiitolene, corresponding to toluene, *i.e.* being methylthiophene, is also known. It boils at  $113^\circ$ , sp.gr. 1.0194. The very minute quantity in which these bodies occur renders them of no industrial importance, even as impurities.

Benzene was first isolated by Faraday in 1825 together with butylene from the liquid condensed in the preparation of lighting gas from whale-oil and other fixed oils and fats as carried out in

London at that time. This process consisted in causing oils to fall drop by drop into retorts made of curved cast-iron tubes heated to a bright red heat. The gas produced was washed in water and immediately compressed into small iron vessels, which were sent out to consumers. The process was invented and perfected by Messrs. P. & J. Taylor between the years 1816 and 1819. They found that 1 gallon of whale-oil gave them 90 cubic feet of gas; Accum, who also experimented with their process, obtaining 105 feet.

The process was probably not in any way altered when Faraday worked on the 'oil' found in the cylinders in which the gas had been compressed. About 1 gallon of this oil was yielded by 1,000 feet of gas. After removing the butylene a mixture was left which did not boil below  $85.5^\circ$ . This was cooled to  $-18^\circ$ , when benzene crystallised out (Faraday, T. 1823, 440). The crystals were separated by draining, pressing on filter-paper, refusion, resolidification, and hydraulic pressing, from an oil which was not very carefully examined, and to which a doubtful formula was assigned, but which was probably a mixture of the higher homologues of benzene.

It is unnecessary here to describe the processes by which Mitscherlich, D'Arcet, Kopp, and many others obtained benzene, as the first practically industrial process was that of Mansfield, founded entirely at first on Faraday's, and dealing with a similar product as the source, namely, coal tar (Mansfield, C. J. 1, 244, 1818). Mansfield took the lower boiling portion of coal tar, which was then used under the name of naphtha for lighting purposes, and distilled it over a flame in a still provided with a jacketed head and a simple form of dephlegmator made by connecting the upper part of the condensing worm with the still body by an inclined tube. The water in the jacket round the long egg-shaped head partially condensed the vapours rising from the boiling fluid until it reached a temperature of  $100^\circ$  when those vapours condensable at that temperature were alone affected and returned to the still, those requiring a lower temperature passing on to the worm, and being condensed and collected. Much of the spray carried upward by the vapours was stopped in the head, and what passed it and was condensed in the connecting tube between the still head and the worm flowed into the inclined tube, and found its way back to the body of the still. Finally, when nothing more could pass the boiling water in the jacketed head, this inclined tube, on a cock being fully opened, which during the first part of the process was partially closed, could be made use of to distil over the higher boiling portions.

Such an apparatus could of course only effect a rough separation of the oil into a 'benzol' mainly distilling below  $100^\circ$  and a 'naphtha' most of which would not distil below  $100^\circ$ .

If, however, the water of the water jacket round the head were carefully kept at a stated temperature, say  $80^\circ$ - $82^\circ$ , a much purer product could be obtained. For some years the process was only carried out with the object of getting oils for the Read Holliday lamp, and for the use of rubber manufacturers.

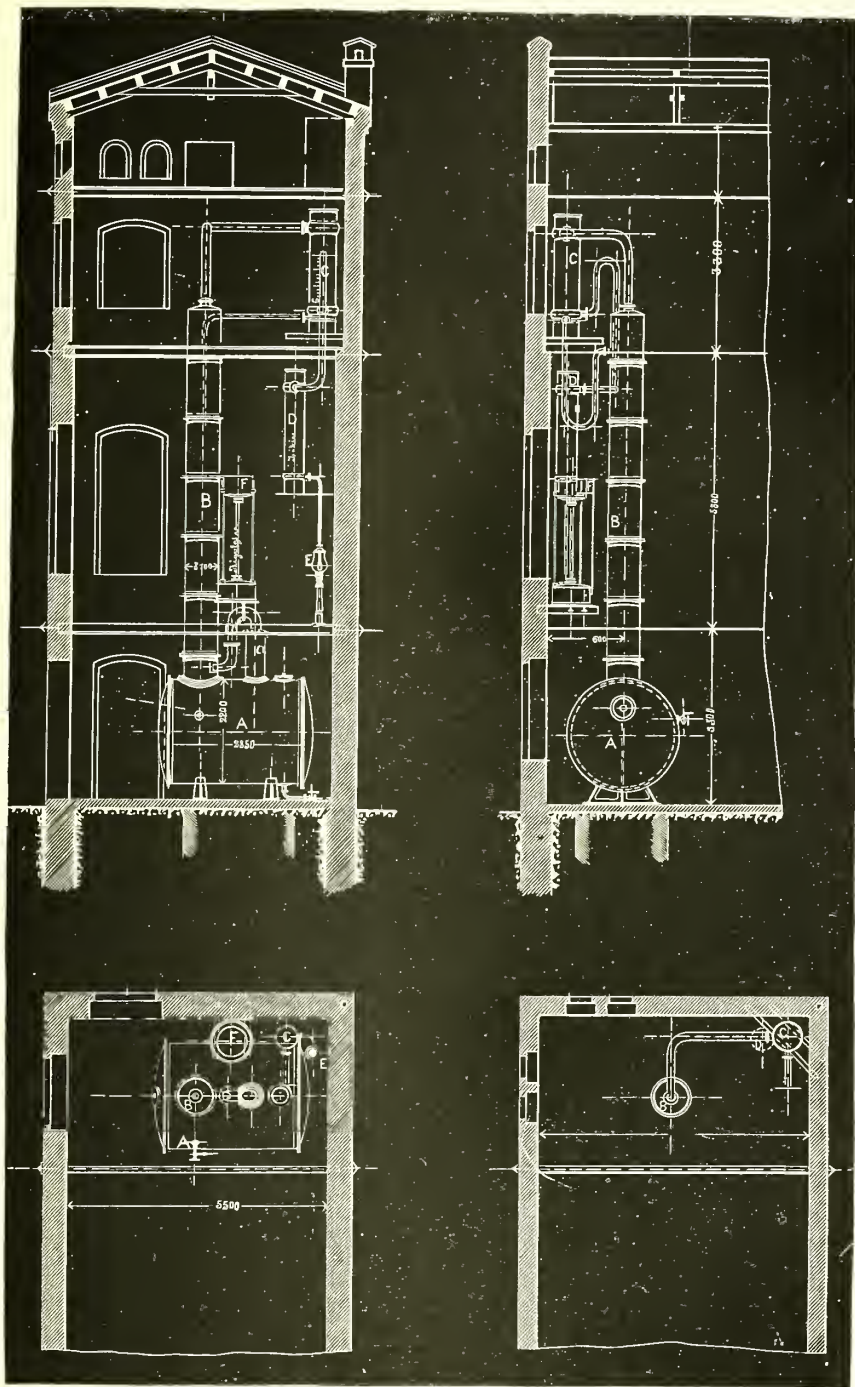


FIG. 1.

A, Still body. B, Analysing column. C, Cooler kept at temperature of distillate wanted. D, Condenser for pure distillate. E, Vase into which distillate flows. F, Automatic regulator.

The early demands for 'benzol' for use in the aniline colour industry were confined to what were known as 30 p.e., 50 p.e., and 90 p.e. benzols, which terms were understood to mean that 30, 50, or 90 p.e. by measure of the sample boiled below 100 C. Of these the 30 p.e. was mainly used for the production of aniline for red, and the 90 p.e. for aniline for blue. Mansfield had, however, subjected his distillates to a careful but most laborious fractionation in glass retorts, finally obtaining perfectly pure benzene by recourse to freezing and pressure, and he pointed out that 'it is evident that any of the summary processes of rectification which are practised by distillers in the manufacture of alcoholic spirits are applicable to the separation of benzole from the less volatile fluids of the naphtha' (Reports of the Royal College of Chemistry, 1849, 257).

Mansfield, in fact, in the remarkable paper just quoted, laid the foundations of the whole benzene industry, and his processes with scarcely a change are in use to this day. The departures from them have been one by one abandoned in favour of his method of absolute separation of the light oils into their constituents, and it is not too much to say that had it not been for his terrible death<sup>1</sup> in February, 1855, we should have had the pure hydrocarbons in the market many years ago.

The introduction of the aniline black printing processes and other improvements in the dye industry, however, slowly gave rise to a demand for a purer benzene, while later on a demand for toluene and xylene stimulated the improvement of the distillation process.

The movement was naturally, as Mansfield had suggested, towards the use of such a still as had been introduced by Mr. Coffey in his patent of 1832 and subsequently carried to great efficiency by succeeding generations of spirit distillers. Coupier of Paris appears first to have worked on a large scale in this direction about 1863. He modified the original Mansfield apparatus in the way mentioned above and showed that at one operation he could separate ordinary 50 p.e. commercial benzol as follows:—

100 litres yielded :

44 litres between 80° and 82° ('Pure benzol')	
6 " " 82° and 110° ('Crude toluol')	
17 " " 110° and 112° ('Pure toluol')	
5 " " 112° and 137° ('Crude xylol')	
9 " " 137° and 140° ('Pure xylol')	
13-14 " " 140° and 150° ('last runnings')	

In addition there were about 6 litres between 62° and 80° consisting of various impurities such as carbon disulphide, acetonitrile, &c.

Vedlė, Savalle of Paris, and others followed with various improvements in the same direction, Savalle being most generally considered to have produced the best still, though it had two very great drawbacks, viz. it was manufactured of copper, which made it very costly, and it was hampered, as far as its condensation arrangements were concerned, by an expensive and useless attempt to use air from a fan driven by steam as a means of cooling the condensers.

The latter attempt was soon given up and we give here a sketch of the apparatus in its

latest form as made by the Metallwerke vormals T. Aders, of Magdeburg-Neustadt.

The still being charged with the proper quantity of naphtha or crude benzol, which has undergone the necessary washings with sulphuric acid and soda lye, steam is admitted into the coils, where it circulates, the condensed water escaping through another tube in the usual fashion. As soon as the liquid begins to boil the vapour ascends into the head *a* and passes through the curved tube *a'* into the bottom of the column, *b*. This contains 25 to 30 flat diaphragms each pierced with a number of small holes, and one larger into which is fitted a short wide overflow tube, the end of which stands up about 2 inches above the level of the plate. On the opposite side of the plate is a small depres-

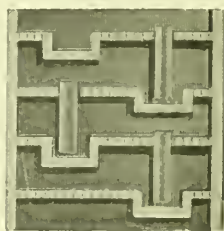


FIG. 2.

sion about 2 inches deep and 4 in diameter, into which the overflow tube from the plate above dips, its own tube dipping in the same way into a depression in the plate below. The condensed fluid acts to each overflow tube as a trap and prevents the ascent of vapour through it.

The rising vapour condenses rapidly on these plates, and the fluid thus produced, unable to penetrate the small holes through which the hot vapour is rushing, rises to the brim of the overflow tube, and then pours down from plate to plate into the still body. The non-condensed vapour rises through the perforations of the next plate, where it undergoes a similar operation, and so on to the top, the vapour passing away from which has thus been successively washed by bubbling through some thirty layers of fluid each slightly cooler than the one beneath. Finally the vapour passes through a surface or multitubular condenser *c*, which is provided with a water supply so regulated that its temperature is about that of the boiling point of the liquid required. The liquid here condensed flows back into the column at a suitable point, while the now purified vapour passes on to the second condenser *d*, and is finally completely condensed into the liquid form. Thence it flows into the glass vase *e*, which is fitted on to a stand-pipe communicating with the distributing-pipes which convey it to the store tanks. The fractions taken should now boil as follows. Benzene 80°, toluene 110°, xylene 140°.

If pure products are required, each fraction is washed with concentrated oil of vitriol, and a washing with soda solution follows. The fraction is introduced into a cast-iron vessel provided with a lid with manhole and inlet pipe. Through the centre passes a vertical shaft rotated by mitre geared wheels. The shaft is provided with arms so arranged that the con-

<sup>1</sup> Mansfield was burned to death by the boiling over of a benzene still.



tents can be thoroughly churned up. A good form of apparatus, due to Messrs. F. B. Welch, of Atlantic Works, Manchester, is seen in fig. 3. The details need no description except

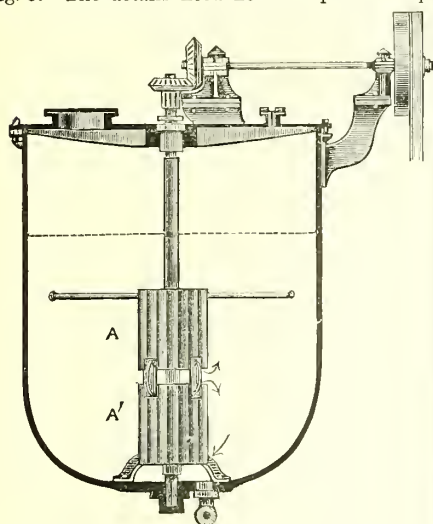


FIG. 3.

to point out that the screws used to force the fluids through the two vomiting tubes A and A' should be set on the shaft with their helices reversed right and left, so that the lower one causes the lower fluid to rush up, and the upper one the upper fluid to rush down; they thus cause the two currents to meet together violently and thoroughly mingle. Air agitation is not advisable on account of the loss of benzol which it is apt to cause.

If the fraction is of fairly good quality and has been properly separated from the crude benzol or light oils, the amount of acid required need not be more than one-twentieth of its weight. In some cases, however, where the impurities are difficult to remove, more must be used and the operation repeated. After the acid has been run off, a washing with enough soda solution to neutralise excess of acid and remove traces of phenols follows, and the fraction is then ready for a second rectification, although if it be benzene or toluene wanted for conversion into aniline in the works where it is made, it can of course be nitrated directly it leaves the acid washer.

If re-rectified, the benzene, toluene, and xylene should have the following boiling-points, which are those of samples made in a large London works:—

	Benzene	Toluene	Xylene
1. . .	81.0	111.8	139.2
2. . .	81.2	111.9	139.5
3. . .	81.2	111.9	139.7
4. . .	81.3	111.9	140.1
5. . .	81.5	111.9	140.3
6. . .	81.7	112.0	140.4
7. . .	81.8	112.0	140.5
8. . .	81.8	112.0	140.6
9. . .	81.9	112.0	140.8
Dry . .	84.0	112.1	141.5

Each fraction 1 =  $\frac{1}{10}$ .

Neither the benzene nor the xylene given above is quite so good as it should be. In really satisfactory samples they should all boil within 0.5 to dryness.

The above boilings were made as described under the article ANILINE, p. 162. 250 c.c. were taken and the thermometer bulb was kept just at the bottom of the neck of the boiling flask; the readings are corrected for barometric pressure. This is not the usual trade method which consists in using a retort and immersing the bulb of the thermometer almost to the bottom of the boiling fluid. One continental maker prescribes for his purchases that the boiling-points shall be taken with the thermometer bulb in the uppermost chamber of a three-bulb rectifying tube. For much information as to the commercial valuation of 'benzols' v. G. E. Davis, *Journal of the Society of Chemical Industry*, iv. 645, also papers by B. Nickels on the impurities of benzol, *Chemical News*, 43, pp. 148, 250; 52, p. 170, and G. Lunge, *Coal Tar and Ammonia*, 2nd edition, 1888.

The treatment for obtaining toluene is exactly the same as that described for benzene, the toluene following the benzene from the crude benzol still and being subsequently re-rectified. Toluene is also accompanied by the corresponding thiophene (thiotoluene) and requires very careful and thorough washing with vitriol or it cannot be got to nitrate properly.

After the separation of the toluene more or less crude xylene is obtained, and the residue in the still is then cooled and run out. When good crude benzol has been worked the residue contains a very large quantity of naphthalene which separates from it when cold, and is known in the works as 'naphthalene salts.' As it has all been brought off from the tar at a low temperature, it is extremely free from higher boiling substances and very pure naphthalene can be obtained from it with little trouble. Of the rest, some 20 to 30 p.c. consists of phenol, to which the same remarks apply. The remaining third consists of a mixture of hydrocarbons from which some more xylene could no doubt be recovered, but the bulk of this 'dead oil,' as it is often called, is used for burning. Metaxylene can be prepared from the purified mixed xylenes by agitation with sulphuric acid, as described for benzene and toluene, to remove the thiophenes, when a subsequent treatment with its own weight of sulphuric acid converts the metaxylene into a sulphonic acid, which after separation from the insoluble portion is hydrolysed, and metaxylene of great purity obtained (C. Häussermann, quoted by G. Lunge, *Coal Tar and Ammonia*, 2nd edition, 476).

*Nitration of benzene, toluene, &c.*—Nitrobenzene first made its appearance in the arts under the name of *essence de myrbane*, manufactured in France by Collas. It was used to scent soap and as a bitter almond flavouring. Mansfield had taken out a patent for its manufacture in 1847, from coal tar benzene. The history of its manufacture is interesting, as the difficulties to be encountered were very considerable.

The first really large quantity produced was made by Messrs. Simpson, Maule, & Nicholson, at Kennington, in 1856. They worked at first

entirely in glass. Along a bench a row of some twenty bolt-heads, each of about 1 gallon capacity, was ranged, with a convenient water trough at hand. Into each flask from 1 to 2 lbs. of benzene was introduced, and the calculated quantity of the mixed acid, divided up into corresponding portions, stood beside each in a stoneware jug. Commencing with the first flask, a workman next proceeded to add a small quantity of the acid and thoroughly swing round and agitate it with the benzene. As soon as he judged it to be safe to leave this flask he treated the next in rotation, and so on till the whole series had received its first portion. He now returned to No. 1 and added a second quantity of acid, and this was continued until all were finished. It need scarcely be said that the process was considered a dangerous one, and that any attempt to increase the scale of manufacture was a very serious undertaking. The attempt, however, was made in cast-iron vessels, furnished with mechanical stirrers, and the size of the apparatus was rapidly increased until it attained dimensions at which it was capable of dealing with several hundred pounds weight of benzene.

The usual arrangement now adopted is as follows:—

A row of vertical cast-iron cylinders, each about 4 feet in diameter by 4 feet deep, is ranged at a convenient height from the ground beneath a line of shafting. Each cylinder is covered with a cast-iron lid, having a raised rim all round. A central orifice gives passage to a vertical shaft, and two or more other conveniently arranged openings allow the benzene, toluene, or xylene, and the mixed acids to flow in. Each of these openings is surrounded with a deep rim, so that the whole top can be flooded with some inches of water without any running into the interior of the cylinder. The lid overhangs the cylinder somewhat, and in the outer rim a number of slots, holes, or tubes allow the water to flow down all over the outer surface of the cylinder into a shallow cast-iron dish in which it stands. By means of a good supply of cold water, the top, sides, and bottom of the whole apparatus are thus kept continually flooded and cooled. The agitators consist of cast-iron arms keyed to the vertical shaft, with fixed arms or dash-plates secured to the sides of the cylinder. The shaft has a mitre wheel keyed on at the top, which works into a corresponding wheel on the horizontal shafting running along the top of the converters. This latter is secured to a clutch, and there is a feather on the shaft, so that any one of the converters can, if necessary, be put either in or out of gear. This arrangement is necessary, as riggers and belts, either of leather, cotton, or rubber, are useless in the atmosphere of the nitrobenzene house. Above, and close to each converter, stands its acid store-tank of iron, or preferably, stoneware. This is often in duplicate, or else the single tank has two or more running-out cocks.

The building should consist of one storey only, with a light gabled roof consisting of rafters on to which pantile laths are secured by good oak trenails. To these either pan or flat tiles should be fixed, either with trenails, or better, the tiles may be of the self-fixing form. The walls should be of hard brick, and the floor

of concrete, nine to twelve inches thick. This, when thoroughly dry, may be coated thinly with good pitch, thinned down with dead oil and put on warm, so as to soak in and protect the surface from the action of the acids.

The floor should be sharply inclined to a drain, which should pass through a large catch-pit or cesspool, which will save any nitrobenzene which might be spilled.

The entrances should be few and of moderate size, provided with stout oak doors; and in addition to the usual fire hydrants there should be means of filling the room with steam from a two-inch pipe, the cock of which is placed without. The building should be completely isolated from the benzene store, nitrate of soda, coal stores, &c.

The charge of acids is always mixed beforehand and thoroughly cooled before use. The nitric acid should have a sp.gr. of 1.388 (1 gram-molecule  $\text{HNO}_3$  per 100 grams weight of acid) and should be free from lower oxides of nitrogen. The sulphuric acid should have a gravity of 1.845 (= 95–96 p.c.  $\text{H}_2\text{SO}_4$ ). A good nitrating mixture consists of 100 parts by weight of nitric to 140 of sulphuric acid, which mixture will serve for 78 parts of benzene or 128 of nitric acid to 179 of sulphuric acid for 100 parts by weight of benzene.

The benzene (in continental works about 100–200 lbs. weight only) having been previously introduced into the converter, the water is turned on, and the cooling apparatus being found in working order, the agitators are set running, and the acid cock turned on so as to allow it to flow in a very thin stream. Should it be necessary to check the machinery even for a moment, the acid should be first shut off and the agitation continued for some minutes, as the reaction proceeds with such vigour that, if the benzene undergoing nitration comes to rest and the acid stream continues to flow, local heating sufficiently great to cause the charge to inflame may speedily occur. Accidents from this source are or have been not uncommon.

The operation lasts for from eight to ten hours, the agitation and cooling being kept up without intermission. When the last portion of the acid has been added the water is shut off, and the temperature allowed to rise somewhat, some manufacturers allowing it to attain close upon  $100^\circ$ . When the temperature ceases to rise the agitators are thrown out of gear and the mixture allowed some hours to cool and settle. The acid is then drawn off and the nitrobenzene well washed with water, and it is then ready to be transferred to the aniline factory. In some works it is distilled for a short time with wet steam, in order to recover a little unconverted benzene and a trace of paraffins, together about 0.5 p.c.

In most English works very much larger quantities than here mentioned are nitrated at one operation, from 100 to 200 gallons of benzene or from 880 to 1,760 lbs. weight being a usual charge. The steam distillation also is seldom resorted to unless the nitrobenzol is to be sold as 'myrbane,' in which case this treatment is essential, and the whole of the substance has to be brought over in order to obtain a perfectly clear and transparent body such as the users of

myrbane demand. It is customary to use toluene imperfectly freed from benzene for this purpose, that article being cheaper and yielding a somewhat more fragrant myrbane than benzene alone.

The waste acid from the nitrating process, of sp.gr. 1.6 to 1.7, contains a very small quantity of nitrobenzene in solution, and also if the reaction has been allowed to go too fast, which causes local heating, small quantities of oxalic acid. Neither of these are worth recovery, and the acid is therefore usually run into large cast-iron pots, set on furnaces and concentrated.

The 'black acid' may be used in the manufacture of nitric acid or transferred to the makers of manures. In some works it is used with the iron residues from the aniline stills to make green vitriol.

The treatment adopted with toluene and xylene is in all essential particulars the same as with benzene.

*Dinitrobenzene and dinitrotoluene* are obtained by treating a charge of the hydrocarbon with double the proportion of the mixed acids, the operation being carried out in two stages, and the second charge of acids run in directly after the first. The cooling water is shut off and the temperature allowed to rise rapidly. Or nitrobenzol already manufactured may be taken and again treated with the necessary acid. Great quantities of acid fumes and some nitro- and dinitro-products come off at the high temperature which is attained, and a good condensing apparatus of stoneware must be used to prevent loss.

The product of the reaction is separated from the acid as usual, and then thoroughly washed with cold, and lastly with hot, water. As dinitrobenzene is sensibly soluble in the latter, the hot washwater had better always be preserved and used for first washing a subsequent batch. Finally, it is allowed to settle, and, while still warm, run out into iron trays, in which it solidi-

fies in masses two to four inches thick. The principal product of the reaction is metadinitrobenzene, m.p. 89.8, but orthodinitrobenzene, m.p. 118°, and paradinitrobenzene, m.p. 172, are also produced, the m.p. of the commercial product being about 85-87. It should not contain any nitrobenzene, and should be well crystallised, hard, and almost odourless, and should not render paper greasy.

Dinitrotoluene is prepared by a process similar to the above, and, since ortho- and paranitrotoluene yield, when nitrated at a high temperature, most of the  $\text{C}_6\text{H}_3\text{CH}_3\text{NO}_2\text{NO}_2$  dinitro-

toluene, it is better to proceed straight on from the toluene.

The subsequent treatment is the same as when dinitrobenzene is manufactured. Commercial dinitrotoluene consists mainly of the last-named and the 1 : 2 : 6 modifications, but always contains small quantities of the other isomers. The 1 : 2 : 6 only occurs in small proportion, and mainly in the oily drainings from the crude product. The nitration of the pure metaxylene does not differ from the processes already described.

R. J. F.

**BENZIDINE** *v.* **DIPHENYL**.

**BENZIDINE-AZO-DYES.** The dyes belonging to this class dye cotton without the aid of a mordant. They are very brilliant, but most fugitive to light, and are prepared by the action of 1 mol. of tetrazodiphenyl, its homologues, the analogous stilbene and fluorene compounds, the azo-compounds of diamidobenzophenone or certain naphthylediamines on the one hand, on 2 mol. of various  $\alpha$ - and  $\beta$ -naphthylaminesulphonic acids,  $\alpha$ - and  $\beta$ -naphtholmono- and disulphonic acids, their alkylised derivatives, or substitution products of benzoic acid on the other hand. The following table shows the influence exercised by the relative positions of the  $\text{N.H}_2 + \text{CH}_3$  groups on the shade of the dye obtained:—

Tetra-derivatives of	Naphthionic acid $\alpha_1-\alpha_2$		$\alpha$ -Naphthol- $\alpha$ -sulphonic acid $\alpha_1-\alpha_2$		$\beta$ -Naphtholdisulphonic acid R	
	Shade	Affinity for cotton	Shade	Affinity for cotton	Shade	Affinity for cotton
Benzidine . . . . .	Yellow-red .	(Congo) .	Blue-violet .	—	Blue-violet .	—
<i>o</i> -Tolidine . . . . .	Red, with tinge of blue .	(Benzopurpurin) .	Blue-violet .	(Azo-blue)	—	—
<i>m</i> -Tolidine . . . . .	Yellow-red .	Small .	Claret-red .	Great .	Red, with blue tinge	Fairly great
<i>p</i> -Tolidine . . . . .	Yellow-red .	Small .	Blue-red .	Small .	Blue-red .	Very small
Xylidine $\text{CH}_3\text{.NH}_2\text{.CH}_3=1:2:3$ .	Orange-red .	Fairly great	Blue-red .	Great .	Blue-red .	Small
Xylidine $\text{CH}_3\text{.NH}_2\text{.CH}_3=1:3:6$ .	Yellow-red .	Slight .	Blue-red .	Slight .	Blue-red .	Very slight
Xylidine $\text{CH}_3\text{.NH}_2\text{.CH}_3=1:2:6$ .	Yellow-red .	Very slight	Yellow-red .	Fairly great	Yellow-red .	Fairly great
Xylidine $\text{CH}_3\text{.NH}_2\text{.CH}_3=2:3:6$ .	Yellow-red .	Slight .	Orange-red .	Fairly great	Red .	Slight
Xylidine $\text{NH}_2\text{.CH}_3\text{.CH}_3=1:3:5$ .	Yellow-red .	Fairly great	Yellow-red .	Fairly great	Red .	Slight
Xylidine $\text{NH}_2\text{.CH}_3\text{.CH}_3=1:2:5$ .	Red, with strong tinge of blue .	Very slight	Violet .	Slight .	Violet .	Slight
Diamido-stilbene . . . . .	—	—	Violet-blue	Great .	—	—
Dimethyldiamido-stilbene . . . . .	—	—	Violet-blue	Great .	—	—

From this table it will be seen (1) That the methyl group only exerts an appreciable influence as regards the shade of the dye when it is in the ortho-position to the amido-group; (2) In the case of the xylidine derivatives the further the second methyl-group in each benzene nucleus is removed from the amido-group, the bluer is the shade of the resulting dye (Weingärtner, Z. 12, 109; Abstr. in S. C. I. 7, 382).

**BENZIDINE BLUE** *v.* **AZO-COLOURING MATTERS.**

**BENZOAZURIN** *v.* **AZO-COLOURING MATTERS.**

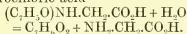
**BENZOIC ACID**  $\text{C}_6\text{H}_5\text{O}_2 = \text{C}_6\text{H}_5\text{CO}_2\text{H}$  (*Acide benzoïque*, Fr.; *Benzoënsäure*, Ger.; *Acidum benzoicum*). Blaise de Vigenère, in his 'Traité du feu et du sel,' published in 1608, described the preparation of benzoic acid by the distillation of gum benzoin. Lemery, in 1675, called attention to its acid properties; and Scheele showed, in 1775, that it could be extracted from gum benzoin by boiling the gum with lime, concentrating the solution, and decomposing the salt



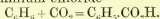
with hydrochloric acid. Schee'e also, in 1785, obtained benzoic acid from cow's urine; but it was not until 1829 that Liebig showed that the substance contained in the urine, by the decomposition of which benzoic acid is formed, is hippuric acid.

*Occurrence.*—Benzoic acid occurs in gum benzoin, tolu balsam, storax, dragon's blood, and various other natural resins; in oil of bergamot and oil of cinnamon; in vanilla, calamus root, and the ripe fruit of the clove tree; in various sweet-smelling flowers—thus in the flowers of *Unona odoratissima*, from which the perfume *ylang-ylang* is prepared; as hippuric acid (and sometimes even, it is asserted, as free benzoic acid) in the urine of herbivora; and in *castoreum*, a viscid, fætid secretion, found in pouches situated in the perinaeum of the beaver.

*Formation.*—By the oxidation of all compounds which contain the phenyl group united to a single lateral chain, such as toluene, benzyl chloride, benzyl alcohol, benzaldehyde, cinnamic acid, &c. By heating benzotrichloride  $C_6H_5.CCl_3$  with water. By heating benzonitrile  $C_6H_5.CN$  with acids or alkalis. By boiling hippuric acid with hydrochloric acid



By passing carbon dioxide into benzene containing aluminium chloride



*Preparation.*—1. *From gum benzoin.* In order to obtain the acid from gum benzoin by sublimation, the gum, broken up into small pieces, is introduced into a flat iron vessel, over the mouth of which filter paper is then pasted. A large conical cap of strong paper, exactly fitting the iron vessel, is placed over the filter paper, tied round the rim, and the whole is gently heated over a sandbath at a temperature of about  $170^\circ$ . The benzoic acid sublimes through the filter paper and collects in colourless crystals inside the paper cone, from which it is removed at the end of the operation (Mohr, A. 29, 177). The yield is about 4 p.c. of the gum employed, and from three to four hours are required for the sublimation of a pound of benzoic acid. A trace of an aromatic oil from the gum adheres to the crystals, imparting to them a pleasant odour of vanilla, and enhancing their value as a pharmaceutical preparation. On a manufacturing scale a modification of the foregoing laboratory process is employed, in which the gum is heated in a closed vessel and the vapour of the subliming acid flows over into a side chamber and condenses at a point below the source of heat, thus obviating all risk of fusing the sublimate. The gum benzoin is introduced by means of a metal drawer, which is heated from beneath by gas jets; whilst the sublimed acid collects in a second drawer and can thus be removed at the end of the operation.

Wöhler's method (A. 49, 245) consists in dissolving the powdered gum in an equal volume of alcohol of 90–95 p.c., adding fuming hydrochloric acid to the hot solution until a precipitate begins to be formed, and distilling the mixture. The distillate contains ethyl benzoate, alcohol, and hydrochloric acid. The residue is again distilled with water as long as ethyl benzoate passes over, and the united distillates are

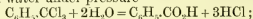
boiled with caustic potash to decompose the ethyl benzoate. From the solution the benzoic acid is precipitated with hydrochloric acid. It smells like the sublimed product.

Scheele's method of extracting the benzoic acid from the gum with slaked lime and water (*v. supra*) may also be employed.

2. *From urine.* The urine of the cow or horse is allowed to putrefy, so as to induce a hydrolytic decomposition of the hippuric acid into benzoic acid and glycocholl. Milk of lime is then added, the filtered solution is evaporated to a small bulk, and the benzoic acid precipitated with hydrochloric acid. In order to avoid the evaporation and the attendant disagreeable smell, the excess of lime may be removed by carbon dioxide, the benzoic acid precipitated by the addition of ferric chloride, and the ferric benzoate, after separating it by filtration, decomposed by hydrochloric acid. The acid thus prepared smells of urine, and must not be used in medicine. The smell may, however, be removed or concealed by mixing the acid with a small quantity of gum benzoin and subliming it.

The fresh urine may also be evaporated to one-third of its bulk, filtered, mixed with hydrochloric acid, and allowed to cool. Hippuric acid crystallises out, which, by boiling with concentrated hydrochloric acid, is decomposed into glycocholl hydrochloride, and benzoic acid.

3. *From toluene.* Most of the benzoic acid employed at the present day, and certainly all that is employed in the coal-tar colour industry, is manufactured from toluene (*v. infra*). Toluene may, by oxidising it with nitric acid, be converted direct into benzoic acid; but it is better to chlorinate it first to benzyl chloride, which is more readily attacked by the oxidising agent. Lunge and Petri (B. 10, 1, 275) boil benzyl chloride (1 part) and dilute nitric acid (3 parts of acid of  $35^\circ$  Baumé with 2 parts of water) with a reflux condenser until the smell of benzyl chloride and benzaldehyde is no longer perceptible. A. v. Rad (D. P. J. 231, 538), however, states that this method is unsuited for preparing the acid on a manufacturing scale, and prefers to decompose benzotrichloride by heating it with water under pressure



but it is difficult to prepare pure benzotrichloride, and the benzoic acid manufactured by this process is always contaminated with chlorobenzoic acids formed from chlorinated benzotrichlorides.

Espenschied (G. P. 47, 187) boils the benzotrichloride with milk of lime, or with a solution of caustic soda mixed with whiting or other insoluble matter, the presence of which aids the reaction by preventing the benzotrichloride from forming a separate layer and also by promoting local superheating.

E. Jacobsen (G. P. 11, 494 and 13, 127) heats benzotrichloride with acetic acid, to which a little zinc chloride has been added

$C_6H_5.CCl_3 + 2CH_3.CO_2H = C_6H_5.CO_2H + 2CH_3.COCl + HCl$ . The acetyl chloride is distilled off, the residue extracted with sodium carbonate, and the benzoic acid precipitated with hydrochloric acid.

The benzoic acid required in the coal-tar colour industry is obtained as a by-product in the manufacture of benzaldehyde by heating benzal

chloride with milk of lime (*v. BENZALDEHYDE*), a portion of the benzaldehyde being converted into calcium benzoate in this process.

**Properties.**—It crystallises in lustrous leaflets or flat needles, melting at  $121.4^{\circ}$ . It boils at  $249^{\circ}$ , but is volatile even at  $100^{\circ}$ , so that it may readily be sublimed; the vapour excites coughing. It may be distilled with steam; 2 litres of aqueous distillate contain 1 gram of benzoic acid. 1,000 parts of water dissolve at

$0^{\circ}$	$20^{\circ}$	$40^{\circ}$	$60^{\circ}$	$80^{\circ}$	$100^{\circ}$
1.70	2.90	5.55	11.55	27.15	58.75

(Boungoin, A. Ph. [5] 15, 168); it is soluble in about twice its weight of ether and in about its own weight of absolute alcohol at ordinary temperatures.

Traces of impurity lower the melting-point of benzoic acid very considerably. The impure acid is also deposited from its solutions in smaller crystals than the pure.

**Reactions.**—When heated with lime, benzoic acid yields benzene and calcium carbonate (Mitscherlich). It is very stable towards oxidising agents; dilute chromic acid is without action on it, but by warming it with manganese dioxide and sulphuric acid it is converted into formic acid, carbon dioxide, and phthalic acid—the latter being formed by the simultaneous oxidation of formic and benzoic acids (Carius, A. 148, 72). Boiling the alcoholic solution with sodium amalgam reduces benzoic acid to benzyl alcohol and other products (Herrmann, A. 132, 75). When distilled over heated zinc-dust it yields benzaldehyde (Baeyer, A. 140, 296). Calcium benzoate yields on distillation benzophenone  $C_{12}H_8O_2$ , together with a small quantity of benzene and anthraquinone  $C_{14}H_8O_2$  (Kekulé and Franchimont, B. 5, 908). Taken internally, benzoic acid is excreted in the urine as hippuric acid (Wöhler).

When a solution of ferric chloride which has been mixed with sufficient ammonia to turn it dark-red is added to a solution of a benzoate, a flesh-colored precipitate of basic ferric benzoate  $(C_6H_5O_2)_3Fe_2Fe(OH)_3$  is formed. This reaction is used in the separation of benzoic acid, and also in separating iron from manganese.

**Uses.**—Benzoic acid is used in medicine; but for this purpose only the natural product, obtained from gum benzoin by sublimation, is suitable. Artificial benzoic acid is employed in the manufacture of aniline blue. It has been used as a mordant in calico-printing. Benzoic acid, dissolved in a mixture of 1 part of ether and 20 parts of alcohol, has been recommended for the preservation of anatomical preparations. It is said to be used in giving an aroma to tobacco.

**Examination of the commercial product.**—The artificial benzoic acid of commerce is almost always contaminated with chlorobenzoic acids (*v. supra*), the presence of which in any considerable quantity is stated to be detrimental in the aniline blue manufacture. The chlorine may be detected by heating the acid with metallic sodium, dissolving the sodium compound in water and testing for chlorine in the solution. The acid should have the proper melting-point and should dissolve without residue in boiling water.

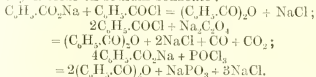
**Salts and ethers of benzoic acid.** Benzoic acid is monobasic. Most of the benzoates are soluble both in water and in alcohol. *Potassium*

*benzoate*  $C_6H_5O_2K \cdot 3H_2O$ : efflorescent laminae. *Sodium benzoate*  $C_6H_5O_2K \cdot H_2O$ : efflorescent needles, used for inhalation in tuberculosis. *Ammonium benzoate*  $C_6H_5O_2(NH_4)$ : rhombic crystals, also used in medicine. *Calcium benzoate*  $(C_6H_5O_2)Ca \cdot 2H_2O$ : lustrous needles, used in the preparation of benzophenone. *Basic ferric benzoate*  $(C_6H_5O_2)_3Fe_2Fe(OH)_3$  (*v. supra*).

The ethers of benzoic acid are obtained either by distilling benzoic acid with the alcohol and sulphuric acid, or better, by saturating a solution of benzoic acid in the alcohol with gaseous hydrochloric acid, digesting the mixture on the water-bath for some hours, precipitating the ether with water and purifying by distillation. *Methyl benzoate*  $C_6H_5O_2 \cdot CH_3$  is a liquid boiling at  $199^{\circ}$ . *Ethyl benzoate*  $C_6H_5O_2 \cdot C_2H_5$  boils at  $212^{\circ}$ .

F. R. J.

**BENZOIC ANHYDRIDE**  $(C_6H_5CO)_2O$ . First prepared by Gerhardt (A. Ch. [3] 37, 299) by the action of benzoyl chloride on sodium benzoate or on sodium oxalate, or of phosphorus oxychloride on sodium benzoate:



**Preparation.**—Pour 100 grams of phosphorus oxychloride over 500 grams of dry sodium benzoate contained in a flask; complete the reaction by heating to  $150^{\circ}$ ; remove sodium salts by washing the cooled mass with dilute sodium carbonate, and purify the anhydride by distillation.

Anschtütz (A. 226, 15) heats benzoyl chloride with anhydrous oxalic acid. This avoids the formation of metallic salts altogether.

**Properties.**—Rhombic prisms, melting at  $42^{\circ}$  and boiling at  $360^{\circ}$  (cor.). Insoluble in water; readily soluble in alcohol and ether.

**Reactions.**—Water decomposes it very slowly in the cold, more rapidly on boiling, with formation of benzoic acid. Towards ammonia, amido- and imido-compounds, alcohols and phenols, it behaves like benzoyl chloride, replacing by a benzoyl-group a hydrogen atom attached to nitrogen or oxygen. For this reason it is, like benzoyl chloride (*q. v.*), used as a reagent for amido-, imido-, and hydroxyl-groups, and it has the advantage over the latter reagent that no hydrochloric acid, a substance which has a very prejudicial effect on many organic compounds, is liberated during its action.

F. R. J.

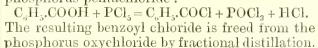
**BENZOIN GUM** *v. BALSAMS*.

**BENZOPURPURIN** *v. AZO-COLOURING MATTERS*.

**BENZOTRICHLORIDE** *v. TOLUENE, CHLORINE DERIVATIVES OF*.

**BENZOYL CHLORIDE**  $C_6H_5OCl = C_6H_5COCl$ . First obtained by Liebig and Wöhler, by passing chlorine into benzaldehyde (A. 3, 262). By the action of phosphorus pentachloride on benzoic acid (Cahours, A. Ch. [3], 23, 334).

**Preparation.**—Benzoic acid is heated with slightly more than the molecular proportion of phosphorus pentachloride:

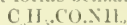


**Properties.**—Colourless liquid, with a pungent odour, boiling at  $198.5^{\circ}$ . Its vapour

X

attacks the eyes, causing a flow of tears. Sp.gr. 1.2122  $\frac{20}{4}$  (Brühl, A. 235, 11).

**Reactions.**—Benzoyl chloride reacts with water, slowly in the cold, rapidly on heating, with formation of benzoic and hydrochloric acids. With ammonia it forms benzamide



together with ammonium chloride. In like manner it reacts with compounds containing hydroxyl, amido-, or imido-groups, introducing benzoyl in place of hydrogen, and is therefore employed in organic chemistry as a test for the presence of these groups in a compound. Thus with alcohol it yields ethyl benzoate; with aniline, benzanilide and dibenzanilide. F. R. J.

**BENZOYL SULPHONIC IMIDE** *v.* SACCHARINE.

**BENZYL BLUE.** A dye made by the Aktien-gesellschaft für Anilinfabrikation, Berlin, by substituting three atoms of hydrogen in rosaniline by three benzyl groups. It is easily soluble in water, dyes silks, wools, and cottons (Reimann's Färb.-Zeit. 1879, 251; Industrie-Blätter, 39, 360).

**BENZYL CHLORIDE** *v.* TOLUENE, CHLORINE DERIVATIVES OF.

**BENZYLDIPHENYLAMINE** *v.* DIPHENYLAMINE.

**BERBERINE.** An alkaloid discovered by Buchner in 1837 (A. 24, 228), in the root of *Berberis vulgaris*, and subsequently found by Bödeker (A. 64, 384; 69, 40) in Colombo root (*Jateorhiza palmata*); by Perrins in *Coscinium fenestratum*, *Hydrastis canadensis*, *Xanthorrhiza apifolia*, and other plants (C. J. 15, 339); and by Stenhouse (Ph. [3] 14, 455) in the bark of *Xylopia polycarpa*.

Fleitmann obtains the alkaloid by extracting the root with alcohol; the extract is evaporated, and the residue treated with water and filtered. The filtrate is neutralised with hydrochloric acid, again filtered, and an excess of hydrochloric acid is added. The chloride is converted into the insoluble sulphate by the addition of sulphuric acid; this is filtered off, decomposed by barium hydroxide, the excess of which is removed by carbon dioxide, and the filtrate is evaporated to dryness; the residue is digested with alcohol, and the berberine obtained by precipitating with alcohol (A. 26, 228).

Lloyd (Ph. [3] 10, 125) isolated berberine from the root of *Hydrastis canadensis* by extracting the powdered root with alcohol, cooling the extract with ice, and precipitating by means of sulphuric acid. The impure sulphate was added to 16 parts of water, rendered slightly alkaline by the addition of ammonia, and then allowed to stand for 24 hours. The liquid was then filtered, cooled by ice, and exactly neutralised with sulphuric acid. From 18 to 20 ounces of the sulphate can be obtained from 100 lbs of *Hydrastis*.

Berberine is obtained from the sulphate by precipitating with ammonia, dissolving the precipitate in alcohol, and reprecipitating by ether.

According to Hesse (B. 19, 3, 190), berberine is accompanied in *B. vulgaris* by four other alkaloids. Parsons (Ph. [3] 13, 46) states that *B. Aquifolium* contains 2.35 p.c. of berberine and 2.82 p.c. of oxyacanthine.

The composition now assigned to berberine is  $\text{C}_{20}\text{H}_{17}\text{NO}_4$  (Court a. Schmidt, B. 16, 2, 589).

It is insoluble in ether and chloroform, soluble in  $4\frac{1}{2}$  parts of water at 21°C., and is moderately soluble in alcohol. The sulphate is orange-yellow, and is soluble in about 100 parts of water (Lloyd, *loc. cit.*). The hydrochloride is soluble in about 500 parts of water, almost insoluble in cold alcohol, ether, and chloroform; its sp.gr., according to Clarke, is 1.397 at 19°C., whilst that of the platino-chloride is 1.758 at 19°C. (B. 12, 1,399).

Berberine on oxidation yields, according to Fleitmann (A. 59, 60), oxalic acid; Weidel (B. 12, 410) could not obtain oxalic acid, but found berberonic or pyridine-tri-carboxylic acid  $\text{C}_8\text{H}_5\text{N}(\text{COOH})_3$ ; whilst Schmidt (B. 16, 2, 589), with alkaline permanganate, isolated hemipic acid  $\text{C}_{10}\text{H}_9\text{O}_2.2\text{H}_2\text{O}$ , melting at 165°C., and which, according to W. H. Perkin, jun. (C. J. 1888), is identified with that obtained from narcotine.

By dry distillation with 5 times its weight of caustic potash, Bernheimer (G. 13, 342; C. J. [2] 46, 340), obtained ammonia, quinoline, and two acids previously described by Hasiwetz.

By treatment with a limited quantity of potassium permanganate, W. H. Perkin, jun., prepared an acid  $\text{C}_8\text{H}_5\text{NO}_5$ , m.p. 113°, and two neutral bodies  $\text{C}_8\text{H}_5\text{NO}_4$  and  $\text{C}_8\text{H}_5\text{NO}_3$ .

Berberine may be detected by adding to the suspected solution, evaporated to dryness, 3 drops of a solution prepared by dissolving 1 gram of fused zinc chloride in 30 grams pure concentrated sulphuric acid and adding 30 grams of water, and again evaporating on the water-bath, when a yellow colour indicates its presence (Jorissen, Ar. Ph. [3] 16, 386). Czumpelik (*loc. cit.* [3] 19, 63) uses a similar reaction, but prepares the testing solution with hydrochloric acid. According to Mandelin (J. 36, 1, 612), vanadates, dissolved in sulphuric acid 1:200, give with berberine the following series of colours: blue violet, violet, red violet to red brown.

Used in medicine as a tonic (*v.* BARBERRY ROOT AND VEGETO-ALKALOIDS).

**BERENGELITE.** A bituminous resinous mineral from St. Juan de Berengela, Peru, melting at 100°C., soluble in alcohol and ether. According to Dietrich, specimens from Trinidad and Arica, Peru, contained 71.81 C, 9.95 H, and 18.21 of O (C. C. 80, 559). Used for caulking ships.

**BERGAMOT.** The *Citrus Bergamia*, a variety of citron cultivated in the South of Europe, valued for the essential oil, which may be obtained either by distillation or by expression from the rind of the fruit.

Bergamot oil is best obtained from the rasped rind of the ripe citron. It is of a light yellow colour, and of an agreeable aromatic odour. Sp.gr. 0.8825 at 22°. It solidifies at a little below 0°C. and after long keeping deposits a sediment, *bergaplene*.

**Bergaptene, Stearoptene of Bergamot oil, Bergamot camphor,** the substance precipitated by the oil of bergamot after long keeping. According to Mulder and Olme (A. 31) it crystallises in needles, melts at 206°C., and volatilises without decomposition. It is inodorous and dissolves in boiling water, alcohol, and ether. Strong sulphuric acid colours it red. Heated with nitric acid it yields oxalic acid. Contains



66.2 p.c. C and 3.8 p.c. H. Rational formula unknown.

**BERGMANN'S POWDER.** An explosive composed of 50 parts potassium chlorate, 5 of pyrolusite, and 45 of bran, sawdust, or tan (J. 37, 1,748).

**BERLIN BLACK.** A black varnish drying with a dead surface, used for coating ironwork.

**BERLIN BLUE** or **PRUSSIAN BLUE** v. **CYANIDES**.

**BERNTHSEN'S VIOLET.** *Isothionine. β-Aminoimidiodiophenylimide.* Formed by reducing β-dinitrodiophenylamine-sulphoxide and oxidising the leuco-base with ferric chloride. The hydrochloride crystallises in needles. Dyes reddish violet. Isomeric with *Lauth's violet*. Bernthsen, A. 230, 133.

**BERTHIERITE.** *Iron sulphantimonite* v. **ANTIMONY**.

**BERYLLIUM.** (*Glucinum.*) Symbol Be. At. w. 9.08 (Nilson and Pettersson).

Beryllium occurs as silicate in *phenacite*; as silicate of beryllium and aluminium in *eucrase* and *beryl*; and as aluminate in *crysoberyl*.

It is obtained by the interaction of beryllium chloride and sodium vapours in hydrogen gas, in small bright globules resembling steel in colour and hardness, of sp.gr. 2.1, melting below the fusing point of silver and oxidising superficially before the blowpipe. It has also been prepared in small hexagonal prisms or tables. Powdered beryllium burns brilliantly when heated in air. It dissolves readily in dilute hydrochloric acid, slowly in warm dilute sulphuric acid, and very slowly in hot strong nitric acid, rapidly in potash solution with evolution of hydrogen. It has no action on water even at a red heat.

Beryllium belongs to the group of metals containing zinc, magnesium, and cadmium. It forms a white oxide BeO and a white gelatinous hydrate Be(HO)<sub>2</sub>; a white deliquescent chloride which forms double chlorides with platinum, tin, and mercury, and also forms basic chlorides. A nitrate and phosphate and normal and basic carbonates and sulphates are also known.

**BERZELIITE.** An arseniate of magnesia and lime found at Långbar and Wernland, containing from 58 to 60 p.c. of As<sub>2</sub>O<sub>5</sub>.

**BESSEMER STEEL** v. **IRON**.

**BETAÏNE** v. **VEGETO-ALKALOIDS**.

**BETEL.** A mixture of the leaf of the betel pepper (*Piper Betel*) with the fruit of *Arcea catechu* or betel nut and *clunam* (lime obtained by calcining shells), universally used by the people of Central and Tropical Asia as a masticatory.

**BETEL-NUT.** The fruit of *Arcea Catechu*.

**BETH-A-BARRA WOOD.** A wood imported from the West Coast of Africa, much valued for its toughness and capability of receiving a high polish. The interstices of the fibres are filled with a yellow crystalline substance which can be extracted from the sawdust by heating with distilled water containing a little sodium carbonate, and precipitating the resulting claret-coloured solution with acetic acid. It is purified by repeated crystallisations from 80 p.c. alcohol.

It differs from chrysophanic acid by melting at 135° instead of 162°, and in not forming a compound with alum (Sadtler & Rowland, Am. J. 1881, 22) For tables showing the difference

in the reactions of brasilin, hæmatoxylin, santalin, and beth-a-barra v. Am. J. 11, 49, and W. J. 28, 537.

**BETORCIN** or **β-ORCIN** C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>. A substance obtained by the decomposition of barbatie acid, found in the lichen *Usnea barbata*. It is less soluble in water than orein and gives a deeper crimson colour with hypochlorites. Kostanecki has obtained it by the action of nitrous acid on *m*-amido-*p*-xylenol, thus showing that it is a dihydroxy-xylene having the substituting groups in the positions CH<sub>3</sub>, CH<sub>3</sub>, OH, OH = 1, 4, 3, 5 (Stenhouse & Groves, C. J. 37, 396; Lampartie, A. 134, 248; Mensehutkin, Bl. 2, 428; Kostanecki, B. 19, 2,321).

**BETULA RESIN** v. **RESINS**.

**BEZETTA.** *Tournesol en drapcaux. Schminck-lupochen. Bezetta rubra et carulea.* A dye or pigment prepared by dipping linen rags in solutions of certain colouring matters. Red bezetta is coloured with cochineal, and is used as a cosmetic.

Blue bezetta (*Tournesol en drapcaux*) which is chiefly used for colouring the rind of Dutch cheeses, is prepared at Gallargues, near Nîmes, in the department of Gard, from a euphorbiaceous plant, *Chrozophora tinctoria* or *Croton tinctoria*. The fruits and the tops of the plants are gathered, and the juice being expressed, rags of coarse cloth are dipped into it, then dried, and afterwards exposed to the fumes of mules' or horses' dung. This last operation is called *aluminadou*. The cloths are turned from time to time, to ensure uniform colouration and prevent any part from being exposed too long to the fumes of the dung, which would turn them yellow. They are then dried a second time, again soaked in the juice, mixed this time with urine, and lastly exposed for some time to the action of the sun and wind. The quantity thus manufactured amounts to about 50 tons yearly. The blue of bezetta is reddened by acids like litmus, though not so quickly, but differs from the latter in not being restored by alkalis. According to Joly, the same dye may be obtained from other euphorbiaceous plants, *Chrozophora oblongata*, *C. plicata*, *Croton tricuspidatum*, *Mercurialis perennis*, and *M. tomentosa*. The juice exists in all these plants in the colourless state, and turns blue only on exposure to the air (Handw. d. Chem. 2 [1] 1,030; Gerh. Traité, 3, 820).

**BEZOAR.** This name, which is derived from a Persian word signifying an antidote to poison, was given to a concretion found in the stomach or intestines of an animal of the goat kind, *Capra aegragus*, which was once very highly valued for this imaginary quality, and has thence been extended to all concretions found in animals.

According to Taylor (P. M. No. 186, 36, and No. 186, 192) bezoars may be divided into nine varieties:—1. Phosphate of calcium, which forms concretions in the intestines of many mammalia. 2. Phosphate of magnesium; semi-transparent and yellowish, and of sp.gr. 2.160. 3. Phosphate of ammonium and magnesium; a concretion of a grey or brown colour, composed of radiations from a centre. 4. Oxalate of calcium. 5. Vegetable fibres. 6. Animal hair. 7. Ambergris. 8. Lithofellie acid. 9. Ellagic or bezoardic acid.

Of true bezoars there are three kinds, Oriental, Occidental, and German. The true Oriental be-

zoars found in the *Capra ægragus*, the gazelle (*Antilope Dorcas*), and other ruminant animals, are spherical or oval masses, varying from the size of a pea to that of the fist, and composed of concentric layers of resinous matter with a nucleus of some foreign substance, such as pieces of bark or other hard vegetable matter which the animal has swallowed. They have a shining resinous fracture, are destitute of taste and odour, nearly insoluble in water and aqueous hydrochloric acid, but soluble for the greater part in potash-lye. These characters suffice to distinguish the Oriental bezoars from those varieties which contain a considerable quantity of inorganic matter. There are two kinds of them, the one consisting of ellagic, the other of lithofellic acid. The latter have a more waxy lustre and greener colour than the former, and are also distinguished by their smaller sp.gr., viz. 1.1, while that of the ellagic acid stones is 1.6. They contain, besides lithofellic acid, a substance resembling the colouring matter of bile, and are perhaps biliary calculi. Oriental bezoars are greatly prized in Persia and other countries of the East for their supposed medicinal properties. The Shah of Persia sent one in 1808 as a present to Napoleon. The Occidental bezoars are found in the lama (*Auchenia Lama*) and in *A. Vicuina*. They resemble the Oriental in external appearance, but differ totally in their chemical characters, inasmuch as they consist chiefly of phosphate of calcium, with but little organic matter.

German bezoars, which are chiefly obtained from the chamois or gamsbock (*Antilope rupicapra*), consist chiefly of interlaced vegetable fibres or animal hairs bound together by a leathery coating.

**BICUHYBA FAT** is expressed from the seeds of *Myristica bicuiba* or *M. officinalis*, a plant found in Brazil. The nuts have a wrinkled, easily-broken, dark shell; the kernel is about the size of a nutmeg, red or yellowish-white in colour, with a rancid taste, followed by a bitter after-taste. The seeds contain 59.6 p.c. of fats, the shells contain 2.6 p.c., and the kernels free from the husks 70 p.c. By pressing under a pressure of 300 atmospheres at 50°C., 860 lbs. of nuts yielded 410 lbs. of fat, or 47.56 p.c.

Brandes, in 1833 (A. 7, 52), confounded it with nutmeg butter; Lewy, in 1814 (A. Ch. [3] 13, 450), describes it as a yellowish-white wax, soluble in hot alcohol and melting at 35°; Peckolt (Ar. Ph. 1,577, 158, 258) found it melted at 47.5 and solidified at 25°. He also isolated an acid bicuhybastearic acid, melting at 55°. Noerdlinger (B. 18, 2,617) finds that the fats vary in colour from dark yellow to brown, melt at temperatures between 42° and 45°, and solidify between 32° and 33°. In the shells he finds another wax-like body, only slightly soluble in hot ether, which melts at 71-75°, and solidifies at 71-72°.

It contains a glyceride of myristic acid (Noerdlinger, l.c.) and trimyristin (Will. a. Reimer, B. 18, 2,011), and other substances not yet investigated.

Its use has been suggested in the manufacture of soaps; those made from it have a pleasant cocoa-like smell.

**BIDRY.** An Indian alloy of zinc, copper, and lead, and occasionally tin. Articles of this

alloy, after being turned in a lathe and engraved, are blackened by immersion in a solution of sal ammoniac, nitre, common salt, and copper sulphate. Known also as *Vidry*.

**BIEBRICH SCARLET** *r.* Azo-COLOURING MATTERS.

**BILBERRY.** (Ger. *Heidelbeere*.) The juice of this berry (*Vaccinium Myrtillus*, L.) is used for colouring wines. Andrée (Ar. Ph. [3] 13, 90; B. 13, 582), states that it is impossible to make certain whether the juice has been used for colouring a wine, as the colouring matter of grapes and of bilberries behaves in almost an identical way with reagents. The spectroscopie also fails to distinguish between the two colours. According to Griessmayer (C. C. 8, 381), ammonia turns bilberry juice a brownish-green, nitric acid in the cold blue changing to red and becoming orange on boiling; lead acetate gives a blue precipitate, copper sulphate a violet colour, sodium carbonate a blue-black, and borax an amaranthus red.

**BIRCH BARK.** (*Betula*.) (*Birke*, Ger.; *Boulcau*, Fr.) The inner bark is used in India as a substitute for paper and for lining the roofs of houses (Dymock, P. J. T. [3] 10, 661). A specimen of bark from Friedrichsruh contained 3.98 p.c. easily soluble and 0.97 p.c. difficultly soluble tanning materials, yielding a good bright leather (W. J. 30, 1,206). Contains a crystalline substance termed betulin,  $C_{30}H_{50}O_8$ , which melts at 258°, and sublimes without decomposition.

**BIRD-LIME.** (*Glu.* Fr.; *Vogelleim*, Ger.) Bird-lime, from *Ilex Aquifolium*, was found by Personne to consist, in addition to vegetable débris and water, of calcium oxalate, caoutchouc, and ethereal salts of a solid crystalline substance, *ilicic alcohol*,  $C_{21}H_{40}O$ , m.p. 175°, with undetermined fatty acids.

According to Divers and Kawakita, Japanese bird-lime, made from *I. integra*, contains ethereal salts of palmitic acid, and in very small quantity a semi-solid acid, the calcium salt of which is soluble in ether and in alcohol. Japanese bird-lime also yields two very similar alcohols by hydrolysis, one differing only slightly from *ilicic alcohol*, and termed *ilicylic alcohol*,  $C_{21}H_{40}O$ , m.p. 172°, and another named *mochylic alcohol*,  $C_{21}H_{40}O$ , m.p. 234°, from *mochi*, the Japanese word for bird-lime.

Caoutchouc is also present in Japanese bird-lime to the extent of about 6 p.c., but only minute quantities of oxalates. By distillation bird-lime yields much palmitic acid and a thick oily hydrocarbon,  $C_{25}H_{44}$  (Divers and Kawakita, C. J. 1888).

**BIREEZ.** Persian name for gum galbanum (Dymock, Ph. [3] 9, 1,016).

**BISMARCK BROWN** *r.* Azo-COLOURING MATTERS.

**BISMUTH.** *Bismuth*. (*Etain de glace*, Fr.; *Wismuth*, Ger.) Symbol Bi. At. w. 207.5 (Schneider, Löwe).

*Occurrence.*—Metallic bismuth occurs in small quantities in widely distributed localities, usually with other ores, such as those of cobalt, nickel, copper, silver, lead, and tin. It is found massive, granulated, reticulated or arborescent, associated with arsenic and silver, and occasionally iron.

The principal districts are Adelaide in South Australia, Altenberg, Schneeberg, Annaberg, Marienberg, Joachimsthal, Johanngeorgenstadt, Lölling in Carinthia, Fahlun, Sweden, and New South Wales. In small quantities it occurs at Huel Sparnon, Cornwall, Carrick Fells, Alva, Stirlingshire, and in Bolivia. Alloyed with 64 p.c. gold it occurs at Maldon, Victoria. Alloyed with tellurium it occurs as *tetradymite* in Cumberland. An alloy of bismuth with 3 p.c. arsenic occurs at Palmbaum near Marienberg.

Bismuth sulphide is widely distributed in small quantities, being found in Saxony, Sweden, South Australia, America, and Cumberland. A sulphide of bismuth, copper, and lead occurs as *needle ore*, *aciculite*, or *patrivite*.

As oxide or *bismuth ochre* it is found as a yellow substance, frequently as a coating on other minerals, associated with iron and other impurities, at Schneeberg, Joachimsthal, Beresof in Siberia, and in New South Wales. The principal ore in Bolivia, which is stated by Domeyko to be the richest country in bismuth, is a compact earthy hydrated oxide.

Bismuth occurs as carbonate or *bismuthite*, usually containing carbonates of iron and copper, at Meynae, with antimony, arsenic, lead, iron, and lime; in Mexico, whence it is imported to this country; North Carolina, and other localities.

Bismuth is stated to occur in most sulphurous copper ores in about the same proportions as silver in galena, in other copper ores except the carbonate, and in most samples of commercial copper and copper coins (Field and Abel, C. J. 16, 304, and Field, C. N. 36, 261).

**Extraction.**—At Schneeberg in Saxony the ore worked is principally metallic bismuth occurring in ores which contain silver, lead, tin, and arsenic in gneiss and clay-slate.

The ore, which contains from 7 to 12 p.c. bismuth, is sorted by hand as far as possible from the gangue before treatment. The old method of *liqation* or 'sweating' is still used, but is becoming superseded by smelting processes in which the metal is much more perfectly extracted.

**Liqaion.**—In this process the metal is separated as far as possible from the gangue by melting at a low temperature. The picked ore is broken into pieces as large as a hazel nut, and placed in inclined iron tubes in charges of about 12 cwt., sufficient space being left in the tube for stirring the ore from the upper end (figs. 1, 2, 3). The tubes are closed at the upper ends by plates of iron, and at the lower ends by similar plates containing circular apertures through which the molten metal may run. The ends of the tubes project slightly beyond the walls of the furnace, the upper over a tank and the lower ends over iron crucibles which contain powdered charcoal, and which are gently heated from below by a small charcoal furnace. The tubes are heated so as to cause the metal to flow easily, and in about ten minutes the bismuth commences to pass out into the crucibles, being there covered by the charcoal and thus protected from oxidation. The ore is occasionally stirred with an iron rod from the upper end, and in from thirty to sixty minutes the operation is completed. The residues, *graupen* or *bismuth barley*, are raked from the upper end into the tank, and at once replaced by fresh ore. In this manner only

about two-thirds of the bismuth is extracted. 20 cwt. of ore require 63 cubic feet of wood. The contents of the pots are removed by ladles to moulds and cast into ingots of 25 to 50 lbs. weight.

Sulphurous ores are usually roasted to remove sulphur, and then smelted in with iron (to remove the last traces of sulphur), carbon, and slag. The regulus of bismuth thus obtained

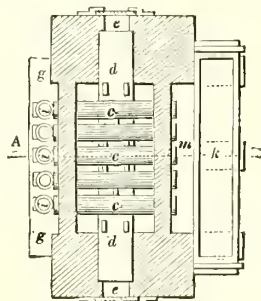


Fig. 1.

is fused on an inclined iron plate and run down, leaving a dross containing much of the impurity. Bismuth ores are sent from Joachimsthal and worked by this process at Schneeberg.

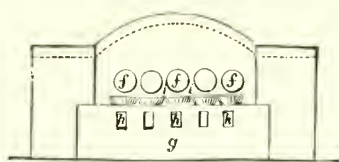


Fig. 2.

The following analyses of two typical samples show the composition of commercial bismuth: From Saxony—Bismuth 99.77 p.c., copper 0.08, silver 0.05, sulphur 0.10; iron trace.

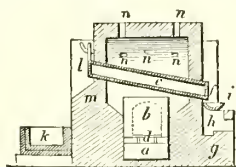


Fig. 3.

From Joachimsthal—Bismuth 99.32 p.c., lead 0.30, silver 0.38; iron and copper traces; sulphur none. About 10,000 lbs. of bismuth are annually produced at Schneeberg.

At Joachimsthal a method devised by R. Vogel is used (D. P. J. 167, 187) for extracting bismuth from ores free from lead. The ores, which usually contain from 10 to 30 p.c. bismuth, are mixed, according to their richness, with 23 to 30 p.c. iron turnings, 15 to 50 p.c. sodium carbonate (according to the amount of gangue present), 5 p.c. lime, and 5 p.c. fluor-spar. The mixture is introduced in charges of about 1 cwt. into clay crucibles, 23 inches high and 16 inches wide at the mouth, covered and heated in a wind furnace to tranquil fusion, and poured into conical moulds. The liquid separates into three layers, the upper consisting of



slag, the second of a speiss containing the arsenic, sulphur, nickel, cobalt, and iron, and most of the other impurities with about 2 p.c. of bismuth, and the lower consisting of a regulus of nearly pure bismuth. The metal is again fused and remoulded (see Kerl, *Handb. der Met. Hüttenkunde*).

A similar process has been adopted by Patera (J. 1862, 646) for the extraction of bismuth from refinery residues.

In France the carbonate of bismuth imported from Meynac is dissolved in the minimum quantity of hydrochloric acid and pieces of iron inserted in the slightly acid liquid. The bismuth is thus precipitated as a black powder, which is well washed and fused in a plumbago crucible under a layer of charcoal at as low a temperature as possible (*Ad. Carnot, A. Ch.* [5] 1, 405, and *Bl.* 21, 114).

For the extraction of bismuth for pharmaceutical purposes from sulphurous ores, Valenciennes roasts the ore on the level bed of a reverberatory furnace for 24 hours with the occasional addition of charcoal and frequent stirring with an iron rabble. When the sulphur has thus been evolved the ore is mixed with about 30 p.c. charcoal, and a mixture of chalk, salt, and fluorspar, and again fused in a reverberatory furnace. From 5 to 8 p.c. of the bismuth is lost by this process, but this is compensated by the extra purity of the product. By subsequent fusion with nitre the antimony, arsenic, and sulphur are removed, and by the ordinary wet methods the lead, copper, and silver are eliminated (*M. A. Valenciennes, A. Ch.* [5] 1, 397). Ores of bismuth averaging 60 p.c. bismuth are imported into England to the extent of about 40 tons annually, principally from Adelaide, S. Australia, and from Mexico. They are usually fused in black-lead pots with borax, sodium carbonate, and a little crude tartar.

H. Tamm (C. N. 25, 85) states that bismuth can be separated from ores containing much copper by fusion with an alkaline flux containing free sulphur, in which case the copper remains unreduced. He recommends a mixture of 5 parts sodium carbonate, 2 salt, 1 sulphur, 1 carbon, to be mixed in about equal proportions with the ore. The bismuth produced is stated to be much more free than usual from arsenic, antimony, and lead, but about 8 p.c. of the total bismuth is lost. The bismuth present in small quantities in lead, copper, and silver ores frequently becomes concentrated in the secondary products of the metallurgical processes and may then be profitably extracted. In the oxidation of silver-lead containing bismuth, the lead oxidises much more rapidly than the bismuth, and at the close of the cupellation a blackish litharge rich in bismuth is obtained, from which that metal may be extracted by reduction and cupellation (J. 12, 711). In this manner bismuth becomes concentrated in the *blacksilver* in the refinement of silver ores at Freiberg, and passes into the hearth bottoms, as much as 25 p.c. being sometimes so absorbed. When the hearths contain sufficient bismuth to be profitably extracted they are finely ground and treated with hydrochloric acid, with the formation of bismuth chloride. Water is added to the solution to precipitate the metal as oxychloride, and the pre-

cipitate is collected, washed, dried, and reduced to metal by fusion with charcoal, sodium carbonate, and powdered glass (*v. Phillips's Metallurgy*).

On the extraction of bismuth from its ores *v.* also Winckler (*Ber. Entw. Chem. Ind.* 1, 953).

*Purification.*—The crude bismuth produced by the above methods contains a variety of impurities from which it is important in many cases to separate it. These impurities are sulphur, arsenic, antimony, copper, nickel, cobalt, silver, lead, and a trace of iron.

Sulphur and arsenic may be removed by fusion with  $\frac{1}{10}$  of its weight of potassium nitrate, with constant stirring at a temperature slightly above the temperature of fusion; the nitre soon oxidises the impurities and a little of the bismuth, forming with them a slag which rises and solidifies at the surface. For the complete removal of these impurities a second fusion is frequently necessary.

C. Méhu (*Ph.* [3] 4, 341) recommends the following process for the removal of sulphur and arsenic. The metal is heated considerably above the melting-point in a vessel so as to expose a large surface, and the oxide is removed to the sides as fast as it forms until about one-fourth of the metal has become oxidised; the greater part of the sulphur and arsenic will then have passed off as oxides. The mass is cooled, pulverised, and mixed with charcoal, dried soap, and potassium carbonate (free from sulphate), about one-fourth of the original weight of the metal, in a crucible, covered with charcoal and heated to redness for one hour. It is thence removed and again fused in contact with air to remove the potassium which it contains, and which separates as a white film on the surface. Arsenic may also be mostly removed by fusion for a considerable time under a layer of charcoal. Arsenic, sulphur, and most of the antimony may be eliminated by fusion at a bright-red heat under borax, stirring with a rod of iron until the action ceases. The iron combines with the impurities and rises as a difficultly fusible slag to the surface, from beneath which the still liquid metal may be poured after partial cooling.

For the complete removal of *antimony*, 2 or 3 parts of bismuth oxide for each part of antimony supposed present are fused with the metal. The oxide of bismuth then gives up its oxygen to the antimony, becoming itself reduced and the antimonious oxide floating on the surface.

Hugo Tamm (C. N. 25, 85) recommends for the removal of *copper* the fusion of the metal at a low temperature under 1 part of a mixture of 8 potassium cyanide and 3 sulphur. When the action has ceased the mass is stirred with a clay (not iron) rod, cooled until the flux has set and the metal poured out from beneath. If impure cyanide is used a relatively larger quantity is required.

*Iron* may be completely removed according to H. Türrach (*J. pr. Chem.* [2] 14, 309) by fusion under a layer of potassium chlorate containing from 2 to 5 p.c. sodium carbonate.

From *silver* bismuth may be separated by cupellation and subsequent reduction of the bismuth oxide so produced, or the metal may be dissolved in nitric acid, the silver precipitated

with hydrochloric acid, the solution filtered, and the basic salt of bismuth precipitated by excess of water, and reduced to metal.

Silver can be partially removed from bismuth by a process resembling Pattinson's process for lead (Schneider, J. pr. [2] 23, 75).

For the separation of *gold* and *silver* E. Matthey (Pr. 42, 89, 94) recommends the addition of 2 p.c. of zinc to the molten metal. The mass is gradually cooled and the surface crust removed. This operation is repeated, whereby the whole of the precious metals are concentrated in the skimmings. On fusing these in a crucible with borax the gold and silver are freed from impurities by the action of the oxide of bismuth, and sink to the bottom. To separate the last traces of these metals from the slag, it is again fused with bismuth.

*Lead* may be precipitated from a nitric acid solution of the metal by the addition of sulphuric acid, and the bismuth recovered as already described. It may also be separated from the fused metal by repeated crystallisations, the alloy of bismuth and lead melting at lower temperatures than the purer bismuth. E. Matthey has thus by four crystallisations reduced the percentage of lead from 12 to 0.4 p.c. (Pr. 42, 93). For the separation of copper from bismuth which has been previously freed from arsenic, antimony, lead, &c., E. Matthey (Pr. 43, 172) recommends its fusion with bismuth sulphide. The pure metal obtained amounts to 90 p.c. of the crude material, while the remaining bismuth sulphide containing copper sulphide may be re-smelted.

*Chemically pure bismuth* is best prepared by dissolving the commercial metal in nitric acid, decanting from any residue, and adding excess of water, whereby the bismuth is precipitated as basic nitrate, leaving the impurities in solution. The precipitate is well washed by decantation, dried, mixed with black flux or other reducing agent which produces a readily fusible flux, and reduced at a gentle heat in a crucible.

*Properties.*—Bismuth is a greyish white crystalline metal of distinctly red tinge when compared with whiter metals such as zinc or antimony. It is very brittle and easily powdered, and a bad conductor of heat and electricity. Its tenacity is very small, a rod 2 mm. in diameter will just support a weight of 11.19 kilos (Muschbroeck). It forms fine obtuse rhombohedral crystals, which approach very closely to the form of cubes. Bismuth melts at 268.3°C. (v. Riemsdijk and Rudberg) and boils at a temperature between the melting-points of copper and nickel, *i.e.* between 1090° and 1450°C. (Carnelley and Carlton Williams), condensing in laminae. Its sp.gr. at 12°C. is 9.823. Scheerer and Marchand have stated that, on exposure to great pressure, the density of bismuth is *lowered*. W. Spring, however, has shown that the density is thereby *increased*. By exposure of bismuth of density 9.804 to a pressure of 20,000 atmospheres the density was raised to 9.856; a second compression still further increased the density to 9.863 (B. 16, 2, 721). It is stated that by careful hammering its density may be raised to 9.88.

Bismuth expands in cooling. Tribe (C. J.) has shown that this expansion does not take place until after solidification.

Exposed to dry air bismuth remains unaltered at the ordinary temperature, but in moist air or in contact with water it becomes coated with oxide. When heated in air it burns with a bluish flame evolving yellowish fumes of oxide. At high temperatures it decomposes water.

Cold sulphuric acid has no action, but the hot concentrated acid dissolves bismuth. Hydrochloric acid acts but slowly. Nitric acid, dilute or strong, dissolves it readily with the formation of nitrate. Powdered bismuth thrown into chlorine gas ignites with the formation of trichloride. It also unites directly with bromine, iodine, and sulphur.

When comparatively pure, bismuth crystallises readily. To obtain it in the form of fine crystals it is melted and allowed to cool until a crust has formed; the crust is pierced on opposite sides with a hot iron, and the still liquid portion poured through one of the openings. On careful removal of the crust the sides of the vessel are found covered with crystals, frequently resembling hollow pyramidal cubes like those of salt, but which are in reality obtuse rhombohedra. Their iridescent lustre is due to a very thin film of oxide which shows the colour characteristic of thin plates.

Bismuth is the most diamagnetic substance known, a bar of the metal placing itself equatorially between the poles of a magnet, *i.e.* at right angles to the position taken up by a bar of iron. Bismuth also occupies an extreme place in the thermo-electric series, being used with antimony in the preparation of the most delicate thermopiles.

*Analysis.*—All compounds of bismuth when mixed with carbon or other reducing agent and fused before the blowpipe give a *brittle* white bead of metal and a yellow incrustation on the charcoal darker than that of oxide of lead.

Salts of bismuth in solution give on addition of excess of water a white precipitate of basic salt, which is insoluble in tartaric acid, and blackens with sulphuretted hydrogen (distinction from antimony).

Metallic iron, copper, lead, and tin precipitate metallic bismuth from solutions.

*Estimation.*—The substance, if in the solid state, is dissolved in nitric acid, diluted slightly (not sufficient to produce a precipitate), filtered if necessary, and precipitated as carbonate by the addition of ammonium carbonate in excess. The liquid is heated nearly to boiling and left for some hours in a warm place, filtered, washed and dried. The precipitate is removed as far as possible from the paper and placed in a porcelain crucible. The paper is ignited on the crucible lid and the crucible and contents ignited and weighed with the lid. The yellow residue is bismuth trioxide  $\text{Bi}_2\text{O}_3$  and contains 89.66 of metal. In presence of hydrochloric acid the above method cannot be used directly, as the precipitate would then contain bismuth oxychloride which is partially volatile and would also render the ignited residue of uncertain composition. It is necessary in that case to precipitate the bismuth with sulphuretted hydrogen, filter off the sulphides, oxidise the precipitate with the filter paper in a beaker by digestion with nitric acid, filter and precipitate with ammonium carbonate and proceed as above. Or

the precipitated oxide containing oxychloride may be reduced with potassium cyanide as described later, and weighed as metal.

From metals which are not precipitated by the addition of chlorides or of excess of water, bismuth may be separated as follows (Rose):—

The solution, if strongly acid, is nearly neutralised with soda or ammonia and a solution of sodium chloride added, followed by excess of water; the bismuth is thus precipitated as oxychloride. The solution is allowed to stand 24 hours; a further addition of water should create no turbidity. The precipitate is filtered, washed with cold water, dried and fused with 5 parts of potassium cyanide in a porcelain crucible at a gentle heat. The mass is boiled with water, filtered, and the metallic particles of reduced bismuth washed, dried, and weighed. Iron, if present, would be precipitated with the bismuth by this method.

Bismuth may be separated from other heavy metals, except lead, in the following manner: To the acid solution sodium carbonate is added in excess, followed by a solution of potassium cyanide. A gentle heat is applied for some time and the precipitate filtered and washed. Bismuth and lead are thus precipitated as carbonates whilst the other metals remain in solution. For the removal of lead this precipitate is dissolved in nitric acid, treated with sulphuric acid and evaporated until fumes of sulphuric acid appear; the solution is then diluted and the lead sulphate filtered off. The bismuth may be precipitated from the solution as oxychloride and treated as before described. From zinc, iron, and other metals not precipitated by sulphuretted hydrogen in acid solution, bismuth may be separated by that gas and the precipitated sulphide dissolved in nitric acid and precipitated as above.

For the dry assay of bismuth ores the fluxes used must depend on the composition of the ore. Thus with ores containing metallic bismuth or that metal as oxide, sulphide, carbonate, &c., a flux consisting of a mixture of 2 parts potassium or sodium carbonate, 1 part sodium chloride, and a proper quantity of argol or potassium cyanide or charcoal powder, will be useful (Tamm); with the addition, where much earthy matter is

present, of borax. Where much copper is present Tamm advises the use of one part of the ore mixed with one part or less of a mixture of sodium carbonate 1, salt 2, sulphur 2, charcoal powder 1 part. The exact proportions in which these fluxes are most useful must be learned by experience.

#### Alloys of Bismuth.

Bismuth unites readily with most metals, forming alloys which are usually of great hardness, brittleness, and fusibility, and most of which expand on solidifying.

*Lead* containing very little bismuth is toughened without becoming more brittle. The addition of bismuth to lead increases its hardness and tenacity; the alloy of 3 lead and 2 bismuth has ten times the hardness and twenty times the tenacity of lead. The alloy of 66 lead and 34 bismuth is very ductile, melting at 166° C.; it corresponds to BiPb. An alloy containing equal weights of the two metals is brittle, of foliated texture, and of the colour of bismuth. Its density is 10.709 *i.e.* greater than the mean density of the constituents.

*Tin.* The addition of bismuth to tin in small quantities renders it more elastic and sonorous. An alloy of 54 tin 46 bismuth is crystalline and brittle; it melts at 133° C. (Guthrie, T. 5, 17, 461). The alloy of 24 tin 1 bismuth is somewhat malleable, but a further addition of bismuth renders it brittle.

*Tin and Lead.* The alloys of bismuth with these two metals are of especial interest. They are extremely fusible, and on account of their expansion on cooling they take a very fine impression, being largely used for electrotypes moulds, &c.

An alloy of 1 bismuth 2 tin 1 lead is used as a soft solder by pewterers, and for the cake moulds for toilet soap. An expensive but effective alloy for stereotype clichés and metallic writing pencils contains 5 bismuth 2 tin 3 lead; it melts at 91.66 C. (199 F.). The varieties of *fusible metal* contain these three metals with the addition sometimes of cadmium, which still further lowers the melting-point. A table of the most important of these alloys is given below:

Name of Alloy	Bismuth	Lead	Tin	Cadmium	Mercury	Melting point	Temperature of Maximum Density
Newton's . . .	50	31.25	18.75	—	—	94.5° C.	—
Rose's . . .	50	28.10	24.1	—	—	95°	55° (Spring)
D'Arcet's . . .	50	25.0	25.0	—	—	94° (Hannay)	—
D'Arcet's with } mercury	50	25.0	25.0	—	250.0	45°	—
Wood's . . .	50	25.0	12.5	12.5	—	65°	25° (Spring)
Lipowitz's . . .	50	26.9	12.78	10.1	—	65°	38.5° ( , , )
Guthrie's 'Eutectic'	50	20.55	21.10	14.03	—	{ stated to have the lowest melting-point }	

The action of heat on fusible metal is somewhat anomalous. Taking Lipowitz's alloy as a typical example, we find (from Spring's table of densities at different temperatures) that this alloy whilst cooling contracts very rapidly at the solidifying point (65 C.); contracts slowly

from that temperature to 38.5°, expands thence to about 25°, and again contracts, occupying at 0° the same volume as at 46° C.

For this reason, in taking a cast or impression with fusible metal it is advisable to allow the alloy to cool to a pasty mass before placing in



the mould. (V. further, Godefroy, Fremy's *Encycl. Chimique*, art. Bismuth, 1888, 24-30.)

*Copper* containing small quantities of bismuth is red short. Traces of bismuth are usually present in commercial copper (Field, C. N. 36, 261). The two metals unite at a temperature below the melting-point of copper, forming hard, brittle alloys of the mean densities of the constituents (Gelert). An alloy of 1 copper 2 bismuth expands considerably after solidification; 1 copper 4 bismuth produces a red crystalline metal.

*Antimony* unites in all proportions with bismuth. The alloy of equal parts of the two metals expands considerably on solidification.

*Mercury* dissolves a considerable amount of bismuth without solidifying. The amalgam containing 1 bismuth and 4 mercury adheres strongly to smooth surfaces such as glass. One part bismuth and 2 parts mercury forms a pasty amalgam. The alloy consisting of D'Arcet's alloy and mercury (*v.* preceding table) is used, on account of its low melting-point, for taking casts of anatomical preparations. The alloy is introduced in the liquid state, allowed to solidify, and the fleshy parts dissolved by solution of caustic soda. This alloy is also used for silvering glass tubes, &c.

*Silver* has a strong affinity for bismuth. An alloy of equal parts of the two metals has the colour of bismuth, is lamellar, and has a density of 10.709, *i.e.* greater than the mean of the constituent metals (Muschelbroeck).

The alloy of *cadmium* 40.8 parts, bismuth 59.2 parts, melts at 144°C. (Guthrie).

Bismuth alloys with the *alkaline metals*; thus, by fusing 5 bismuth with 4 cream of tartar (hydric potassic tartrate) an alloy of bismuth and potassium is produced, which becomes tarnished in air, has an alkaline reaction and taste, and evolves hydrogen when plunged in water.

A. H. Gallatin (*Ph. M.* [4] 38, 57) has prepared an alloy of bismuth with *ammonium*. He scattered ammonium chloride over bismuth sodium alloy and added water. The alloy swelled and again contracted. On plunging in water or heating, a mixture of hydrogen and ammonia was evolved. After drying *in vacuo* over sulphuric acid, it evolved 27 volumes of gas on heating.

Bismuth combines very imperfectly with iron, forming alloys of diminished density. With platinum, palladium, gold, and tellurium it also forms alloys. Compounds with the two latter metals occur in nature.

#### COMPOUNDS OF BISMUTH.

Bismuth forms three classes of compounds in which it occurs as a diad, triad, and pentad respectively. The trivalent compounds are the most stable.

**Oxides.** Four oxides of bismuth are known, but the trioxide and the compounds derived from it are the only ones of commercial application.

**Bismuth trioxide**  $\text{Bi}_2\text{O}_3$  occurs in nature as *bismuth ochre*. It is best prepared by the ignition of the subnitrate of bismuth until red fumes cease to be evolved. It may also be prepared by igniting the metal at a red-white heat in a muffle. The metal then burns and forms the oxide, which condenses as a yellow powder. Bismuth oxide is a pale-yellow amorphous sub-

stance which melts at a red heat to a glass without change of weight. Its specific gravity is 8.21; it contains 89.66 p.c. bismuth.

It is used for glass and porcelain staining; as an addition to certain fluxes to prevent the production of colour, and in gilding porcelain, being mixed in the proportion of 1 part oxide to 15 parts of the gold.

The darkening of the commercial substance on exposure to light is due to the presence of a trace of silver.

A **hydrated bismuth oxide**  $\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$  is precipitated as a white powder on addition of caustic alkali to a bismuthous salt, such as the nitrate. It dissolves in alkali in presence of glycerine. On addition of sugar to the solution metallic bismuth is precipitated, while arsenic, if present, remains in solution. Löwe (Fr. 22, 498-505) recommends this method for the preparation of pure bismuth for pharmaceutical purposes.

**Bismuth nitrate**  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  is prepared by dissolving bismuth or its oxide or carbonate in moderately strong nitric acid. The concentrated solution is filtered, if necessary, through asbestos, and deposits on cooling large deliquescent crystals, which are caustic, and melt in their water of crystallisation when gently heated.

When the bismuth used for the preparation contains arsenic, excess of nitric acid should be used for the solution, the arsenic is then oxidised to arsenic acid, and combines with its equivalent of bismuth, being precipitated as arsenate of bismuth. R. Schneider (J. pr. 20, 418-434) recommends the following proportions: 2 kilos bismuth, 10 kilos *hot* nitric acid (75° to 90°C.); when the action is finished the liquid is decanted from the sediment, which contains all the arsenic. On addition of water to the solution a white precipitate of basic nitrate falls, the constitution of which varies with the amount of water used. This was formerly known as *magistery of bismuth*, and is now called *flake* or *pearl white*, the latter name being also applied to the oxychloride of bismuth.

For pharmaceutical purposes the subnitrate is prepared as follows: Dissolve 2 parts of bismuth in 4 parts nitric acid, add 3 parts water, pour from deposit, if any, evaporate to one-third the bulk, and pour into 80 parts of water, filter, wash and dry the precipitate at a temperature not above 55°C.

It is a pearly-white powder consisting of minute crystalline scales. It is employed as a flux for certain enamels, augmenting their fusibility without imparting any colour, and on this account is used as a vehicle for metallic oxides. For the colourless iridescent glaze on porcelain the basic nitrate is rubbed with resin and gently heated with lavender oil; by the addition of coloured oxides, yellow and other colours are produced. It is also used like the oxide and in the same proportions for gilding porcelain, and to some extent as a cosmetic under the names *blanc de fard* and *blanc d'Espagne*. It is largely used in medicine.

When prepared from impure metal it is liable to contain arsenic, lead, and silver; tellurium has also been suspected (Ph. 3. No. 287). To test for arsenic, heat a little of the nitrate in a tube until brown fumes cease to be evolved, add a small crystal of potassium acetate and

again heat; in presence of a trace of arsenic the odour of kakodyl is observed (A. Glenard, *J. de Pharm.* [4] 1, 217).

**Bismuth chloride**  $\text{BiCl}_3$ . This compound is produced when finely powdered bismuth is thrown into chlorine gas or when chlorine is passed over the heated metal. It is also formed by the solution of bismuth in aqua regia and evaporation of the liquid.

It is a white, easily fusible solid, which absorbs moisture from the air, forming a crystalline hydrate. By the addition of water a white precipitate of basic chloride or oxychloride is produced corresponding to  $\text{BiOCl}$ , though its composition varies considerably.

The oxychloride of bismuth is, however, usually prepared by pouring a solution of the normal nitrate into a dilute solution of common salt, forming oxychloride of bismuth and sodium nitrate.

It is a white pearly powder known as *pearl white*, and is used as a pigment, and in the preparation of a very fine yellow pigment known as Merimée's antimony yellow (*v. ANTIMONY*).

**Bismuth chromate** *v. under CHROMIUM*.

**BISMUTHITE**. Native bismuth trioxide. The most abundant and widely diffused ore of bismuth. A form found in spheres of darker or lighter brown, the size of peas, and frequently inclosing a grain of bismuth, is known as *Bismuthospharite*; a specimen analysed by Weisbach, *J. M.* 1882, 2, 254 contained 91.68  $\text{Bi}_2\text{O}_3$ , 8.29  $\text{CO}_2$ , and traces of  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ . Its sp.gr. was 7.61.

**BISSA-BOL** *v. GUM RESINS*.

**BISTRE** *v. PIGMENTS*.

**BITTER ALMOND OIL** *v. BENZALDEHYDE*.

**BITTER APPLE** *v. COLOCYNTH*.

**BITTER SWEET** *v. DELCAMARA*.

**BITTER WOOD** *v. QUASSIA*.

**BITTERN**. The mother liquor which remains after the crystallisation of common salt from sea-water, or the water from salt springs. It contains soluble magnesium salts, bromides and iodides. The same term is also applied to a mixture of equal parts of quassia extract and sulphate of iron, 2 parts extract of cocculus indicus, 4 parts Spanish liquorice, and 8 parts treacle, used to sophisticate beers (Cooley, 1).

**BITUMEN**. This term includes a considerable number of inflammable mineral substances consisting mainly of hydrocarbons. They are of various consistence, from thin fluid to solid, but the solid bitumens are for the most part liquefiable at a moderate heat. The purest kind of fluid bitumen, called naphtha or rock oil, is a colourless liquid of sp.gr. 0.7 to 0.81, and with a bituminous odour. It often occurs in nature with asphalt and other solid bitumens. Petroleum is a dark-coloured fluid variety containing much naphtha. Maltha or mineral tar is a more viscid variety. The solid bitumens are *asphalt* (*q. v.*); *mineral tallow* or *hatchetin*; *elastic bitumen*, *mineral caoutchouc* or *elaterite*; *ozokerite*, &c.

An abundance of bitumen is found in the island of Trinidad at the Pitch Lakes, and in Mexico. It is supposed to be a product of the decomposition of vegetable matter, and consists chiefly of hydrocarbons with variable quantities of oxygen and nitrogen, *v. PETROL*.

**BITUMINOUS COAL** *v. FUEL*.

**BIXEIN, BIXIN**. Colouring matters of Annatto, *v. ANNATTO*.

**BJELKITE or COSALITE**. A mineral containing—

Bismuth . . . .	42.40	39.40
Lead . . . .	40.30	37.61
Iron . . . .	1.01	5.13
Sulphur . . . .	16.29	17.83

Sp.gr. 6.32–6.75 (*J.* 30, 1, 270).

(Sjögren, *J. M.* 1879, 611; *J. C. S.* [3] 40, 688.)

**BLACK AMBER** *v. AMBER*.

**BLACK AZO- or NAPHTHOL BLACK** *v. AZO-COLOURING MATTERS*.

**BLACK BAND IRONSTONE** *v. IRON ORES OF*.

**BLACK BOY GUM** *v. BALSAMS*.

**BLACK CHALK**. A kind of clay containing carbon, found in Camarvonshire and in the Isle of Islay.

**BLACK COPPER** *v. COPPER*.

**BLACK EARTHY COBALT** *v. COBALT*.

**BLACK FLUX** *v. ASSAYING*.

**BLACK HELLEBORE ROOT**. (*Radix Hellebori nigri*, *Racine d'Ellebre noir*, Fr.; *Schwarze Nieswurzel*, Ger.)

The root of the *Helleborus niger* (Linn.) or Christmas Rose, Woodville (*Med. Bot.* 169), Bentl. a. T. (*Med. Plants*, 2). Black hellebore and the nearly related green hellebore, *Helleborus viridis* (Linn.), are seldom employed in England except in veterinary medicine. They are both powerful intestinal irritants.

Vauquelin (*Ann. de Muséum*, 8, 87), Soubeiran (*N. Traité de Pharm.* 1), and Feneulle and Capron (*J. Ph.* 8, 503) examined hellebore, but no definite constituent of physiological importance was announced till the discovery of *helleborin* by Bastick in 1852 (*Ph.* 12, 174). Our knowledge of the chemistry of hellebore is, however, chiefly due to Husemann and Marmé (*A.* 133, 55) who show that besides helleborin  $\text{C}_3\text{H}_2\text{O}_6$ , which is a glucoside, there exists in both the black and green hellebore another glucoside, *helleborein*,  $\text{C}_3\text{H}_4\text{O}_{13}$ . Helleborin exists in greatest quantity in the *niger*, but it is also the chief of the two constituents in the *viridis*.

Helleborin when purified consists of groups of microscopic needles which crumble in the air to a yellowish-white hygroscopic powder. It has a sweet taste. Darkens at 220–230°. Water and alcohol dissolve it, but it is insoluble in ether. Sulphuric acid forms with it a brownish-red solution which changes to violet. By the action of dilute acids it breaks up into *glucose*, and a grey-green amorphous precipitate of *helleboretin*,  $\text{C}_3\text{H}_2\text{O}_6$ . Helleborin likewise assumes the form of white shining needles. Melts with decomposition at 250°. It is insoluble in cold water, slightly soluble in ether; but easily soluble in boiling alcohol or chloroform. It gives a characteristic and delicate colour reaction with sulphuric acid. The crystals become deep-red and dissolve in the acid to a deep-red solution. The taste of helleborin is acrid and burning. Dilute acids break it up into *glucose* and a resinous substance, *helleborein*,  $\text{C}_3\text{H}_4\text{O}_{13}$ . Helleborein is insoluble in water, slightly soluble in ether, but is readily dissolved by boiling alcohol.

A. S.

**BLACKING.** (*Cirage*, Fr.; *Schuhwicksse*, Ger.)

Blacking, as we now use it, was introduced from Paris in the reign of Charles II., and owing to the general and still increasing demand for it as a polish for boots and shoes, is now an important branch of industry.

A liquid blacking may be prepared by mixing 16 parts of bone-black and 2 of sperm oil in a wooden or stoneware vessel; 12 parts of treacle are then gradually added, and the whole is beaten together until a perfectly homogeneous mass is obtained, 3 parts of oil of vitriol diluted with three times its bulk of water is added in small quantities at a time, and the mass allowed to stand, with a good stirring daily for several days. 1 part of gum in 48 of vinegar is then added gradually, the whole is stirred briskly for some time, and then daily for 3 or 4 days.

Several other methods of making blacking are described in Cooley's Encyclopedia. The following are the processes that have been recently described:—

150 parts of wax and 15 parts of tallow are dissolved in a boiling mixture of 200 parts linseed oil, 20 parts litharge and 100 parts of molasses; the whole is heated to 120°, 103 parts of black are added, on cooling it is diluted with 280 parts of oil of turpentine and mixed with a solution of 5 parts gum lac and 2 of aniline violet in 55 parts of alcohol (Nicolet, Ger. Pat. 19,048, December 1881).

90 parts beeswax or ceresine, 30 parts spermaceti, 350 parts oil of turpentine are melted and then mixed with 10 parts of borax, 20 parts black, 10 parts Prussian blue, and 5 parts nitrobenzol (Heim, Ger. Pat. 19,279, February, 1882; S. C. I. 1, 404).

Ganthner's varnish is prepared by adding 3 parts of wax and 2 of castor oil with sufficient pigment to a filtered solution of 80 parts shellac in 15 alcohol. The whole is evaporated in vacuum to the consistency of syrup (Ger. Pat. 19,267, December 1881).

Brunner makes a blacking by stirring well together 10 parts of bone-black and 10 parts of glucose syrup, and then adding with rapid stirring 5 parts sulphuric acid. 2 parts sodium carbonate are next dissolved in 4 parts of water, and boiled, with constant stirring, with 20 parts of train oil, till a thick liquid is obtained, the acid solution is then mixed with it with rapid stirring (Chem. a. Drug. 26, 233).

Kilner's blacking for ladies' shoes, 2 oz. shellac, 1 oz. liquid ammonia, 8 oz. water; boil, add sufficient aniline black to colour, and make up to 16 oz. (Chem. a. Drug. 26, 369).

Paste blacking may be prepared by mixing together 2 lbs. ivory-black, 1 of treacle, 4 oz. of sperm oil, 5 of vinegar, and 5 of sulphuric acid, and adding to the mixture  $\frac{1}{2}$  oz. ferrous sulphate and  $3\frac{1}{2}$  oz. of gum arabic dissolved in 5 oz. of water. By using more vinegar and less bone-black, liquid blackings can be manufactured (Chem. a. Drug. 26, 537).

Scholz's liquid blacking is made by dissolving 50 grams of asphalt in 50 grams of naphtha and adding 6 parts of linseed oil varnish, 14 of train oil, and 13 of spirits of wine (D. P. J. 242, 456).

In manufacturing liquid blackings, the ivory-black must be in a finer state of division than for paste blackings.

Blackings, both liquid and paste, should be stored in cool, moderately dry cellars. Blackings which are crude, moist, and oily lose these properties and become drier and more brilliant by age. Indeed, it is said that the best boot and shoe makers never use a blacking which they have not had in stock for a twelvemonth.

**BLACK JACK.** The miner's term for blende or zinc sulphide (*v.* ZINC).

**BLACK LEAD.** The common name of plumbago or graphite (*v.* CARBON).

**BLACKLEY BLUE** *v.* INDULINES.

**BLACK LIQUOR.** Ferrous acetate (*v.* ACETIC ACID).

**BLACK TELLURIUM** *v.* TELLURIUM.

**BLACK TIN** *v.* TIN.

**BLACK VARNISH.** *Black Japan* (*v.* VARNISH).

**BLACK WAD** *v.* MANGANESE.

**BLACK, WOOL,** *v.* AZO-COLOURING MATTERS.

**BLANC FIXE.** Trade name for ground barium sulphate, used as a pigment.

**BLANQUETTE.** A kind of crude soda, less powerful than barilla, obtained at Aigues-Mortes by the incineration of *Salsola Tragus* and *S. Kali* (Watts, 1).

**BLEASTING GELATINE AND POWDER** *v.* EXPLOSIVES.

**BLEACHING.** This term signifies the art of destroying the natural colour of vegetable and animal products in such a manner as to leave them unimpaired with as white an appearance as possible. The removal of certain other natural or artificial impurities usually accompanies the bleaching proper. The art acquires its greatest importance in connection with the textile fibres, cotton, linen, wool, and silk, hence special reference will be made to the modern methods of bleaching these materials.

**Cotton bleaching.** Cotton is usually bleached in the form of yarn, thread, and calico, very seldom as loose cotton-wool. The natural impurities occurring in raw cotton amount to about 5 p.c. and consist chiefly of pectic matters; other substances present are brown colouring matter and very minute quantities of margaric acid, cotton-wax, and albuminous matter. The soiled grey appearance of raw cotton-wool, yarn, and thread is almost entirely due to the presence of these natural impurities. Cotton cloth or calico, however, is still further contaminated with flour or starch, fatty matter, china clay, and other mineral substances, all of which, to the amount of 30–50 p.c., have been introduced during the sizing of the warp.

**Cotton yarn and thread bleaching.** If the cotton yarn is in the form of warps, these are loosely plaited by hand or machine in order to reduce their inconvenient length; if in the form of 'hanks' these are bleached separately or linked together in chain form; wet yarn is sometimes bleached in the form of 'cops,' *i.e.* ready for the spool of the weaver's shuttle.

The several operations of the bleaching process for 1,500 kilos yarn, employing low pressure kiers, are as follows:—

1. *Ley-boil.* 300 litres caustic soda (sp.gr. 1.16), 2,000 litres water, boil 6 hours; wash in kier 1 hour.





reduced to a minimum, and a regular even singe is the result.

All singeing machines are provided with lever arrangements for immediately removing the cloth from the hot plate, or the gas flame from the cloth, in case of necessity; further danger from fire is avoided by causing the singed cloth to pass at once between a pair of rollers moistened

with water, or through a small steam chamber, in order to extinguish sparks adhering to the cloth.

The above preliminary operations are now succeeded by those of the bleaching proper. The following is an outline of the process at present in use for 24,000 kilos. cloth, employing low-pressure kiers:—

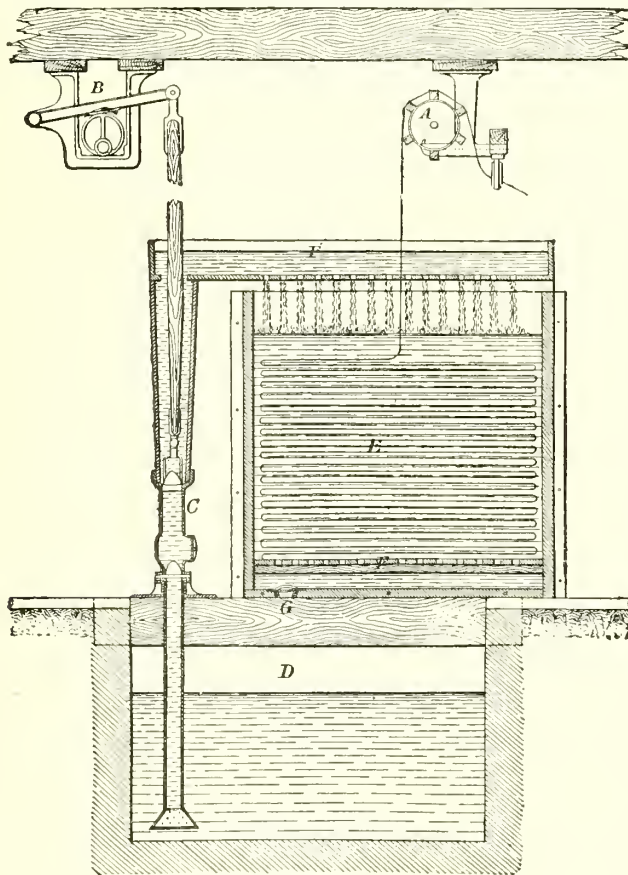


FIG. 2.

1. Wash after singeing.
2. *Lime-boil.* 1,000 kilos. lime, water about 37,000 litres; boil 12 hours; wash.
3. *Lime-sour.* Pass through hydrochloric acid (sp.gr. 1.01); wash.
4. *Ley-boils.* 1st. 340 kilos. soda ash, water about 37,000 litres; boil 3 hours.  
2nd. 860 kilos. soda ash, 380 kilos. resin, 190 kilos. caustic soda (solid), water 37,000 litres; boil 12 hours.  
3rd. 380 kilos. soda ash, water 37,000 litres; boil 3 hours; wash.
5. *Chemicking.* Pass through bleaching-powder solution (sp.gr. 1.0025); pile 2–12 hours; wash.
6. *White-sour.* Pass through hydrochloric or sulphuric acid (sp.gr. 1.01); pile 1–3 hours.
7. Wash, squeeze, open out, and dry.

1. *Wash after singeing.* From the singeing house the cloth is drawn through the washing machine in chain form, then plaited down on the floor and allowed to lie 'in pile' for some hours to soften. By this operation the cloth is well soaked with water, and is thus better prepared to absorb the liquors used in the subsequent operations. Should the cloth be heavily sized, much of the adventitious matter is also removed at this stage.

The form of washing machine generally employed is shown in figures 3 and 4. It consists of a water trough B, above which a pair of heavy wooden squeezing rollers AA are supported. Two chains of cloth are washed simultaneously; they enter the machine at the ends, pass between the squeezing rollers, then round the roller K in the water trough, again between the rollers AA, and thus travel spirally towards

the centre of the machine, whence they are drawn out by a winch and piled on the floor. A constant stream of water from the main *c* enters at the centre of the trough by the tap *e*, the dirty water flowing out at both ends; *c* are wooden guide pegs to separate the several strands of cloth; *ss* are strong brass rings or 'straining eyes' through which the cloth enters the machine, and which can be set at any angle to regulate its tension; *κ* and *w* are the screws, levers, and weights for regulating the pressure of the squeezing rollers against each other. The action of this machine is such that the cloth is continuously being soaked with water and then squeezed, thus causing a vigorous stream of water to flow down the upward moving strands of cloth.

2. *Lime-boil* (lime-bowk, bucking, bowking). The pieces are run through milk of lime supplied to a washing machine of small dimensions—generally termed the 'liming machine'—and are at once drawn by winches into the lime kiers, carrying with them the lime they have absorbed. The cloth is plaited in regular folds and well tramped down by boys who enter the kiers. After adding the necessary amount of water, the boiling and circulation of the liquor takes place as already described in the case of the ley-boil of cotton-yarn bleaching.

The lime-boil has for its object the decomposition of the fatty, waxy, and resinous impurities present in the cloth. Though not removed, but adhering still to the fabric in the form of lime-soaps, their altered condition facili-

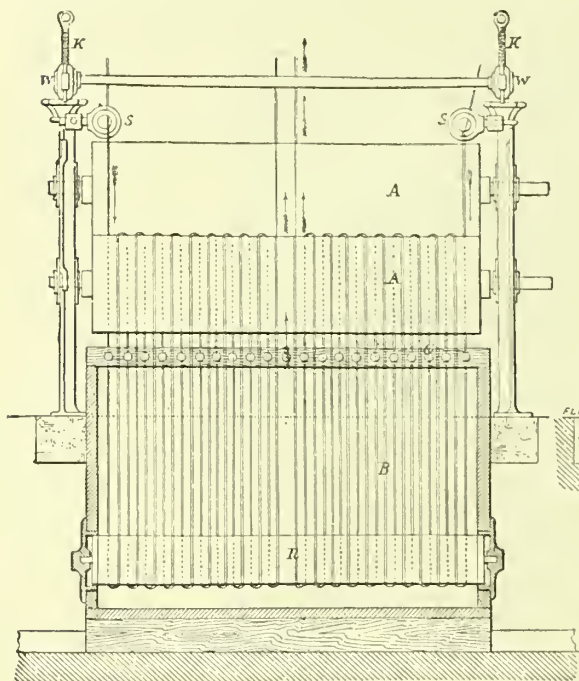


FIG. 3.

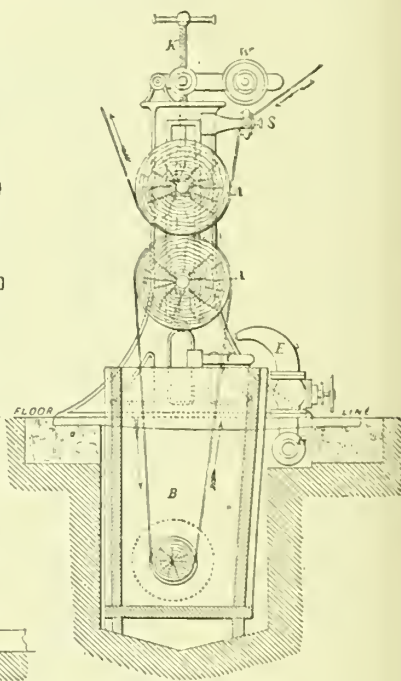


FIG. 4.

tates their removal by the subsequent processes. The starch of the size is removed, and the colouring matter of the fibre is modified. Lime is preferred to caustic soda because it is cheaper, and much more effective in saponifying neutral fatty matter than the caustic or carbonated alkalis; indeed with the exception of barium hydrate it seems to be the most energetic saponifying agent which could be used in cotton bleaching.

It is very essential to have a sufficiency of water in the kier, so that it stands at least about two feet above the false bottom; otherwise the cloth, either at the top or bottom of the kier, is very apt to be tendered, probably because it becomes oxidised by the action of the steam upon the cloth in its limed condition. On the other hand, an excess of water in the kier is to be avoided, since then the cloth is apt to float and become

entangled, or damaged by rubbing against the sides during the boiling. When closed high-pressure kiers are employed, the increase in volume of liquor by the condensation of the steam must be taken into account, and, if necessary, a little liquor must be allowed to escape.

Of the several varieties of kier which have from time to time been introduced in practice, mention may be made of 'Barlow's kiers,' which are still greatly in vogue. These are always worked in pairs, and so arranged that the top of one kier is connected by a pipe with the bottom of the other; the pipes which enter at the top and centre of each kier are continued as perforated pipes or 'distributors' to a little above the false bottom, and then to the bottom of the kier as a stay. Both kiers having been charged with cloth, the necessary amount of water is run into one kier only; high-pressure steam



is then admitted at the top, and the liquor forced out below enters the distributor of the other kier at the top and permeates the cloth. When all the liquor has been thus transferred, the taps are reversed so that the steam forces the liquor in a similar manner back into the first kier. This alternating process and circulation of the liquor is continued for about seven hours.

Pendlebury's arrangement of kiers is precisely similar to that of Barlow, the only difference being that one kier is smaller and serves only to hold the liquor each time it is forced through the

cloth contained in the larger kier. The arrangement is cheaper, more economical as regards space required, and is suitable for small requirements.

In the *vacuum kier* of Mason and others, the circulation of the liquors is effected by means of a pump. After filling the kier with cloth, the air is pumped out and the boiling liquor is then admitted; in this manner a more perfect penetration of the material by the liquor is obtained.

The *injector kier* of Mather and Platt is shown in fig. 5; *A* is the kier filled with cloth,

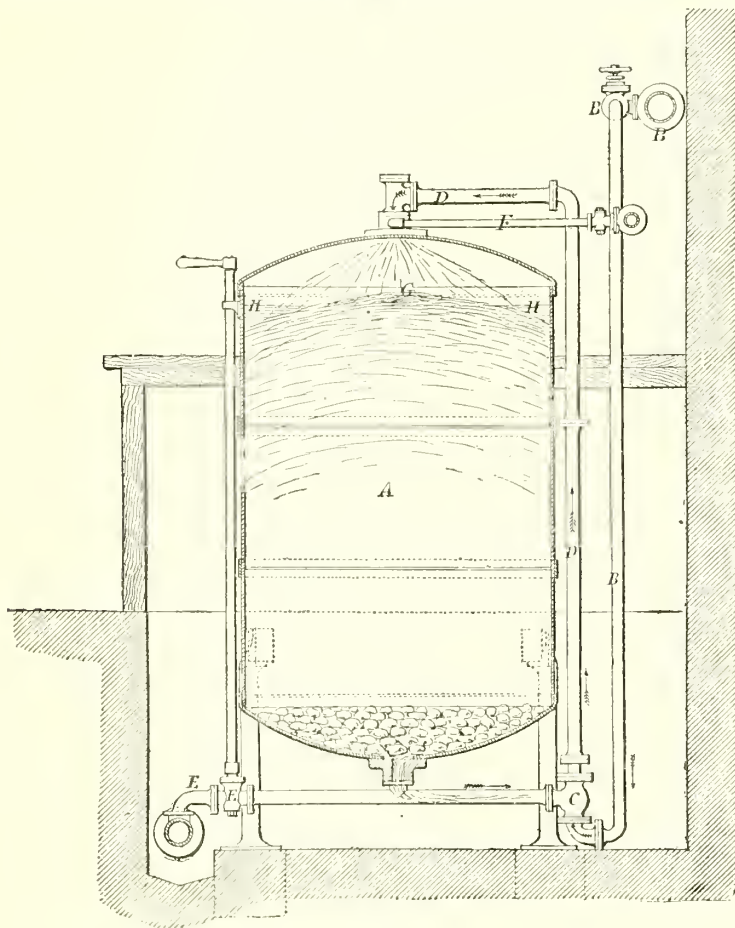


FIG. 5.

*BB* are the steam pipes, *c* is the injector, and *D* the circulating pipe; *F* is the liquor pipe by which water or other liquor is admitted, *EE* is the draw-off valve and waste pipe. When the kier has been suitably filled with cloth and liquor, steam is turned on, and, by the action of the injector *c*, the liquor is withdrawn from the kier below, forced up the pipe *D*, and spread over the cloth at *G*. Temporarily collecting at *H*, the liquor is gradually drawn through the cloth, and in this manner a continual circulation of liquor is maintained.

3. *Lime-sour* (grey-sour). After the lime-boil the pieces are washed, then passed through a washing machine fed with dilute hydrochloric acid, and, if convenient, at once washed.

The object of the lime-sour is to decompose the insoluble lime-soaps fixed on the cloth during the lime-boil, and to dissolve and remove the lime, also any iron or other metallic oxides present. Experiments by A. Scheurer show also that the use of the lime-sour makes it less essential that complete saponification of the fatty matter should take place during the lime.

boil than would be the case if it were omitted. This is so because the free fatty acid liberated during the lime-sour greatly facilitates the saponification of any undecomposed neutral fat during the succeeding ley-boil, since the soap which the fatty acid then forms emulsifies the neutral fat and exposes it to the action of the alkali employed. Hence the adoption of the lime-sour is equivalent to shortening the time of the lime-boil. A continual flow of fresh dilute acid into the machine must be maintained, and, since it is rapidly neutralised by the lime, it is well to ensure a constant slight acidity of the liquor by occasionally making acidimetric tests. Hydrochloric acid is preferred to sulphuric acid because it gives the more soluble calcium chloride. The soured cloth should never be permitted to remain long exposed to air, especially air currents, otherwise the acid is apt to concentrate in the exposed portions and thus tender the fibre.

4. *Ley-boil.* This operation takes place in the same kind of boilers as are used for the lime-boil. The fatty acids resulting from the decomposition of the lime-soaps during the grey-sour, also the brown colouring matters, are removed during this operation. Its special feature is the use of resin-soap, which greatly facilitates the removal of fatty matter by exercising a purely mechanical emulsive action, the alkali present being then able more readily to saponify the emulsified fats, particularly those neutral fats which perchance have escaped the action of the lime-boil. Ordinary soft-soap acts in a similar manner, but resin-soap is cheaper and better. A. Seheurer finds by experiment that, after caustic lime, the most rapid saponification of a neutral fat spotted on a piece of calico is effected, when boiling under pressure at 120°C., by a solution containing 10 grams anhydrous caustic soda and 2½ grams resin per litre. Increasing the amount of resin does not hasten saponification, though this is done by increasing the velocity of the circulation of the solution. Indeed with circulation even a more rapid saponification is effected with caustic soda and resin than with lime.

The preliminary short boiling with soda ash, which is sometimes replaced by merely soaking the cloth with a weak solution of soda ('sweetening'), prevents tendering of the cloth by neutralising any traces of acid left in by reason of insufficient washing after souring. The boiling with soda-ash after the resin-boil is for the purpose of completing the removal of fatty matters and any undissolved resin, which otherwise give rise to brown stains. Immediate removal of the cloth from the kier and washing is necessary to prevent the production of iron stains.

5. *Chemicking.* The application of the bleaching-powder solution takes place in washing machines of the ordinary kind, but provided with stone instead of wooden troughs, because of their greater durability. The bleaching action takes place essentially during the lying-in-pile or exposure to air of the cloth saturated with the solution of bleaching-powder; the carbonic acid of the air liberates hypochlorous acid, and this, in the presence of the fibre, at once decomposes, yielding hydrochloric acid and oxygen: in the moment of its production the oxygen oxidises and destroys the traces of colouring matter

present in the fibre, thus giving it the highest degree of whiteness.

It is necessary to avoid the use of strong solutions of bleaching-powder, otherwise the fibre itself is attacked, oxycellulose being produced; and even if the cotton is not tendered thereby it is still apt to acquire brown stains during subsequent operations employed by the calico-printer, e.g. steaming.

6. *White-sour.* This operation is similar to the lime-sour already described, except that sulphuric acid is usually employed instead of hydrochloric acid, chiefly because of its lower cost. Its object is to decompose and remove traces of undecomposed bleaching-powder, lime, iron, and the oxidised colouring matter.

7. The *final washing* must be as thorough as possible in order to ensure the removal of all traces of acid, which, if left in the cloth, would inevitably tender portions of it during the drying process. After washing, the cloth is specially squeezed by passing through a pair of heavy wooden rollers, or through the modern grooved brass roller and disc machine of W. Birch. The chain of cloth then passes in a horizontal, loosely hanging position, between a pair of rapidly revolving, double-armed winches or scutehers, which effectually shake out the twist from the chain. Thus opened out to the full width, the cloth is dried by passing over steam-heated copper cylinders, and folded. The time usually required to complete the madder bleach is four to five days.

**The market bleach.** In market bleaching the object is simply to give a brilliant white appearance to the calico or other similar material, to fit them for immediate sale in the market as finished white goods. It is not necessary to have the calico well 'bottomed'—i.e. cleansed from all colour-attracting impurities, since no subsequent dyeing or printing is intended. The operations are for the most part identical with those of the madder bleaching process. The modifications introduced are shown in the following outline of the process, intended for 24,000 kilos. cloth, employing open or low-pressure kiers:—

1. *Lime-boil.* 1,440 kilos lime, water about 37,000 litres; boil 12 hours; wash.
2. *Lime-sour.* Hydrochloric acid (sp.gr. 1.01); steep 2-4 hours; wash.
3. *First ley-boil or grey-boil.* 240 kilos caustic soda (solid), about 37,000 litres water; boil 12 hours; wash.
4. *Chemicking.* Bleaching-powder solution (sp.gr. 1.005); steep 2-4 hours; wash.
5. *Second ley-boil or white-boil.* 240 kilos soda-ash, about 37,000 litres water; boil 12 hours; wash.
6. *White-sour.* Sulphuric acid (sp.gr. 1.01); steep 2-4 hours; wash.
7. Tint with blue, squeeze dry.

More or less elaborate finishing operations follow—e.g. starching, calendering, beetling, stentering, &c. Some bleachers introduce a white-sour between operations 4 and 5, and a second chemicking between operations 5 and 6. The absence of resin-soap in the ley-boils is characteristic.

**The Turkey-red bleach.** This is merely a curtailment of the foregoing processes, and is

specially intended for yarn or cloth to be subsequently dyed plain alizarin-red or Turkey-red. In it the operation of singeing and the application of bleaching-powder are omitted, since they diminish the fulness and brilliancy of the Turkey-red dye; the use of the latter is to be avoided, because it gives rise to the production of oxycellulose. The use of resin-soap is unnecessary, and the process is limited to the following operations:

1. Wash.
2. Boil in water 2 hours; wash.
3. *Ley-boils*.  
1st. 90 litres caustic soda (sp.gr. 1.35), about 3,000 litres water; boil 10 hours; wash.  
2nd. 70 litres caustic soda (sp.gr. 1.35); ditto ditto.

4. *Sour*. Sulphuric acid (sp.gr. 1.01); steep 2 hours.

5. Wash well and dry.

The above quantities of materials are intended for 2,000 kilos. cloth, with low-pressure kier.

**The steamer-kier bleaching process.** The bleaching processes previously described have been in vogue with little change during the last forty years; minor modifications have certainly been introduced, but the chief improvements have always been in respect of the mechanical appliances employed. Quite recently (since 1883-84) another most important advance in the same direction has been made, which marks an epoch in the history of bleaching.

In 1883 Thompson patented a bleaching process in which the goods contained in an air-tight kier are submitted to the action of bleaching-powder solution and of carbonic acid alternately. The carbonic acid is drawn from a gas-holder into the kier containing the cloth steeped in bleaching powder solution, by allowing the latter to flow out into a tank below. The bleaching liquor is then pumped back into the kier, thus forcing the carbonic acid which remains, back into the holder.

In 1884 W. Mather, of the firm of Mather & Platt, Manchester, devised an improved arrangement in which the calico could be passed continuously through chambers or tanks containing the two necessary agents mentioned.

In the following year Mather introduced the so-called *steamer-kier*, in which the goods, previously impregnated with dilute caustic soda, were submitted to the action of low-pressure steam.

The so-called *Mather-Thompson* process results from a combination of the two processes here indicated. With regard to the principles of the process there is nothing new, for the application of carbonic acid in connection with bleaching-powder solution was patented by P. F. Didot in 1855, while the steaming of goods impregnated with alkali was patented as far back as 1800 by J. Turnbull.

The novelty consists essentially in the machinery employed, by which the duration of the bleaching process is very much shortened, and other material advantages are gained.

For a *market bleach* with these new appliances, the goods are submitted to the following operations:—

1. *Ley-scour*. Pass through hot dilute caustic soda—or waste soda-liquor from a previous steaming operation; squeeze and wash.
2. *Ley-prepare*. Pass through a boiling solution of NaOH (sp.gr. 1.01-1.02); squeeze and run into steamer-waggon.
3. *Ley-boil (or steam)*. Boil in steamer-kier for 5 hours with 4 lbs. pressure; wash in the kier with hot water for 2 hours; wash in washing machine.
4. *Chemicking*. Pass continuously through a series of vats containing:—  
  1. Hot water.
  2. Bleaching-powder solution (sp.gr. 1.005).
  3. Carbonic acid gas.
  4. Cold water.
  5. Hot solution of  $\text{Na}_2\text{CO}_3$  (1 gram per litre).
  6. Cold water.
  7. Bleaching-powder solution (sp.gr. 1.0025).
  8. Carbonic acid gas.
  9. Cold water.
  10. Hydrochloric acid (sp.gr. 1.01).
5. Wash in washing machine; tint with blue; squeeze and dry.

The following notes explain the above operations more fully:—

*Ley-scour*. The object of this operation is to cleanse the cloth from such superficial impurities as 'size' &c., so that the alkali subsequently applied may, with unimpaired strength, exert its action entirely to remove the natural impurities of the fibre.

*Ley-prepare*. This operation is not strictly necessary, since the impregnation of the fabric with caustic alkali might be effected in the kier itself; but it ensures a more thorough and even saturation of the cloth with alkali. The operations of 'scouring' and 'preparing' are performed by passing the cloth through roller-vats containing the necessary solutions. Excess of liquor is removed by squeezing rollers, and the cloth, containing about one and a half times its weight of liquor, is piled in the steamer-waggons. These waggons are constructed of strong galvanised iron, and form as it were large lattice-work cages or baskets, running on wheels, each capable of holding from one to three tons of cloth. The lattice-work may be dispensed with, and the waggon then assumes the form of a box or vat having one or more perforations in the bottom.

*Ley-boil*. The steamer-kier consists of a strong wrought-iron horizontal boiler, one end of which can be closed by a specially constructed sliding door. At the side of the kier stands a centrifugal pump connected with the top and bottom of the kier, and also with liquor tanks beneath, so that either boiling water or dilute caustic alkali solution can be sprinkled on and circulated through the goods. Figs. 6 and 7 show the general disposition of the steamer-kier.

Two waggons of cloth having been run into the kier, and the door closed, steam is admitted till the pressure reaches a maximum of 4-5 lbs. During the steaming or boiling process, a continual sprinkling of the cloth with dilute caustic soda (sp.gr. 1.01-1.02) is maintained,



in order to keep the cloth well saturated with liquid, and thus prevent oxidation and consequent tendering of the fibre by the action of the steam. The excellent circulation of the liquors in the steamer-kier is a noteworthy and most important feature, since it greatly facilitates the saponification of the fatty matters on the cotton.

After steaming, the liquor is run off, the kier is almost filled with hot water, and this is circulated through the cloth by means of the centrifugal pump for one hour. A similar washing with fresh hot water takes place during another hour.

Each kier is provided with two pairs of

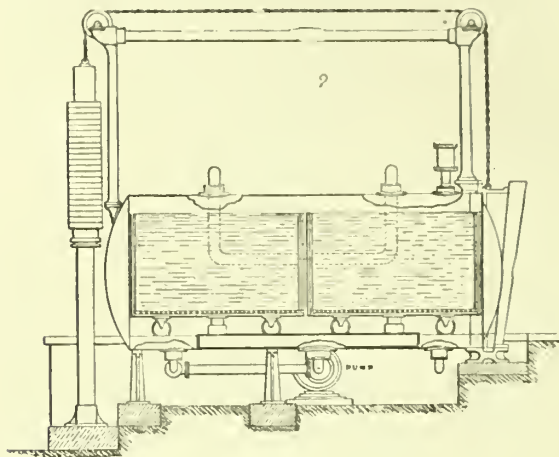


FIG. 6.

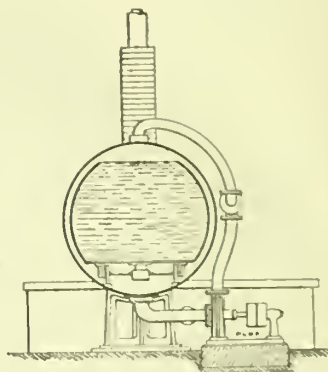


FIG. 7.

waggon, so that while the goods in one pair are being steamed, the other pair can be emptied and refilled with cloth ready to be steamed. In this manner the operation of steaming is rendered as continuous as possible and a very great saving of time is effected.

*Chemicking.* After receiving a thorough wash in the ordinary roller washing machine, the pieces are passed through a series of vats provided with rollers above and below, and containing the several agents already enumerated. This continuous bleaching range is

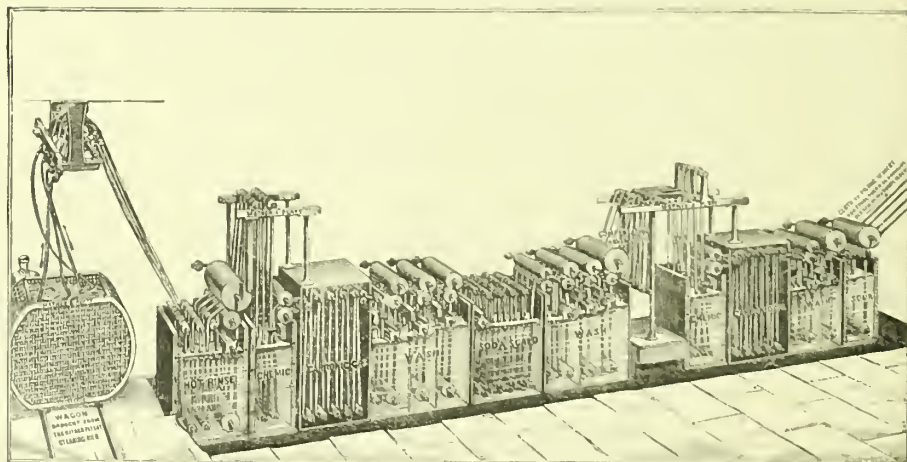


FIG. 8.

shown in fig. 8. Thin goods are ran through in chain form, thick ones may be run in the open width.

The bleaching-powder solution is led continuously to the chemic vats from a high-level tank. The carbonic acid is prepared from marble and hydrochloric acid in a special

apparatus, and conducted by underground pipes to the closed chambers of the bleaching range.

The pieces pass through the whole series of vats in about three minutes, running at the rate of about sixty yards per minute.

The duration of the Mather-Thompson bleaching process, from the grey to the white

state, is from ten to twelve hours. According to the patentees, and their statements seem to be corroborated by the reports of various firms who have adopted the process, the saving, compared with the ordinary process of bleaching, is as follows: in value of drugs one-fourth, of labour one-half, of water four-fifths, of coal one-half, of lime two-thirds. Much less space is required, since one steamer-kier can do the work of four ordinary boiling kiers, and the machine operations are reduced one-half. The following details have been furnished by H. Koechlin, of the Loerrach Printworks.

To effect the *madder bleach* by the *steamer-kier* process, the continuous bleach with the application of carbonic acid &c. is omitted, the older method of chemicking and souring being preferred. Those who consider the lime-boil as essential may apply it equally well by means of the steamer-kier.

The operations in this case are as follows:—

1. *Lime-boil (or steam)*. Run through milk of lime, 50 grams per litre, and pile in steamer-waggon; boil in steamer-kier 5 hours at 10 lbs. pressure, circulating 2,000 litres water. Wash in kier with hot water.
2. *Sour*. Sour as usual with dilute HCl (sp.gr. 1.015°); pile 2-3 hours and wash.
3. *Ley-prepare*. Pass through NaOH solution (sp.gr. 1.005-1.01°), heated to 70°C., and pile in steamer-waggon.
4. *Ley-boil (or steam)*. Boil 6 hours in steamer-kier at 10 lbs. pressure, with circulation of resin-soap liquor: 40 kilos soda-ash, 20 kilos resin, 1,000 litres water. Wash four times ( $\frac{1}{3}$ -1 hour each time), with boiling water, and finally with cold water, in kier.
5. *Chemicking*. Pass as usual through dilute bleaching-powder solution (sp.gr. 1.0025°); wash.
6. *Sour*. Pass as usual through dilute sulphuric acid (sp.gr. 1.01°); wash and dry.

Perfectly satisfactory results, however, are obtained by even *omitting* the lime-boil and proceeding as follows:—

1. *Sour*. Pass as usual through dilute  $\text{H}_2\text{SO}_4$  (sp.gr. 1.015°); pile 2-3 hours; wash and squeeze.
2. *Ley-prepare*. Pass through following solution at 70°C.: 20 litres bisulphite of soda, sp.gr. 1.3; 20 kilos. NaOH (solid 72 p.c.), 1,800 litres water; pile in steamer-waggons.
3. *Ley-boil (or steam)*. Boil in steamer-kier 6-8 hours at 10 lbs. pressure, with circulation of resin-soap liquor: 20 kilos NaOH (solid 72 p.c.), 40 kilos soda-ash, 20 kilos resin, 2,000 litres water; wash 4 times ( $\frac{1}{3}$ -1 hour each time), with boiling water, and once with cold water in kier.
4. *Chemicking*. As above.
5. *Sour*. As above; wash and dry.

With the exception of the employment of the steamer-kier and the use of bisulphite of soda, this process is essentially the same as that

employed for many years with success by Messrs. Guillaume Frères of St. Denis.

The preliminary souring process effects the decomposition of any insoluble fatty acid compounds present in the grey cloth; it removes calcareous or other mineral matter soluble in acids, and modifies any starchy matter present, probably rendering it more soluble. The addition of the small proportion of the reducing agent bisulphite of soda, along with the caustic soda in the preparing process, is intended to prevent any oxidation and consequent tendering of the cotton during the steaming process. The use of resin-soap along with the caustic soda, combined with the perfect circulation of the liquor, is very material to the success of this the shortest modern method of madder bleaching, for reasons already stated.

According to H. Koechlin, this method gives a perfectly satisfactory bleach. The dye is not permanently stained in an alizarin dye-bath, and does not become yellow on steaming.

A noteworthy recent invention of Dr. G. Lunge is the application of acetic acid in connection with bleaching-powder, in place of mineral acids or carbonic acid. It can be applied immediately before or after, or even along with the solution of bleaching-powder. It liberates hypochlorous acid with formation of soluble calcium acetate. When the hypochlorous acid exercises its bleaching power, it gives up oxygen and produces hydrochloric acid, which immediately acts upon the calcium acetate. In this manner the acetic acid is reproduced, and is thus ready to decompose fresh portions of calcium hypochlorite.

A solution of sulphurous acid has been used by some bleachers for the final souring process in place of sulphuric acid, over which it possesses the advantage of being an antichlor, in consequence of its reducing action.

A passing reference may be made to the so-called *electrical bleaching processes* of Hermite and others, the sole feature of which is that the bleaching liquid (hypochlorite) is furnished by passing an electric current through solutions of calcium or magnesium chloride, or other similar salts. They are all more or less in an experimental stage, and the results obtained are such that one cannot reasonably expect to see bleaching-powder replaced in the near future by any electrically produced bleaching liquid.

The history of cotton bleaching may be briefly said to comprise the following noteworthy improvements:—

1. The use of chlorine gas by Berthollet in 1787, and of hypochlorite of lime in 1799 by Tennant.

2. The boiling with carbonate of soda instead of caustic soda, after the lime-boil, introduced from America about 1837. A more effectual decomposition of the lime-soaps was thus obtained.

3. The adoption of the lime-sour as proposed by A. Scheurer-Rott in 1837.

4. The use of resin-soap in the ley-boils about the same period.

5. The introduction of high-pressure boiling kiers about 1844.

6. The use of caustic alkali and resin-soap in conjunction with the steamer-kier, to the exclusion of the lime-boil, in 1883-84.

**Linen bleaching.** Since the retted flax fibre contains a much larger proportion of natural impurities than cotton, e.g. 25-30 p.c. pectic acid, beside fatty matter &c., linen is not so readily bleached as cotton. In the main, however, the methods adopted for the two fibres are the same. Linen is bleached in the form of yarn, thread, or cloth.

**Linen-yarn bleaching.** Very frequently linen yarn is only partially bleached, the process being completed, if necessary, when the yarn has been woven into cloth.

The following operations are employed in order to obtain 'half-white' or cream, with 1,500 kilos yarn, using low-pressure kiers:

1. *Ley-boil.* Boil 3-4 hours in solution of 150 kilos soda-ash; wash and squeeze.
2. *Chemick (Reel).* Reel 1 hour in bleaching-powder solution, sp.gr. 1.0025°; wash.
3. *Sour.* Steep 1 hour in dilute sulphuric acid, sp.gr. 1.005°; wash.
4. *Ley-boil (Scald).* Boil 1 hour in solution of 30-75 kilos soda-ash; wash.
5. *Chemick.* Reel in dilute solution of bleaching-powder, sp.gr. 1.0025°; wash.
6. *Sour.* Steep 1 hour in dilute sulphuric acid, sp.gr. 1.005°; wash well and dry.

If the yarn should be bleached more completely, then operations 4, 5, and 6 are repeated two or three times, as may be found necessary, with this difference, that between 4 and 5 the yarn is 'grassed,' i.e. exposed in the field to the action of the air, light, and moisture, for several days. By introducing this very gentle method of bleaching, the full strength of the fibre is better maintained.

The various operations are conducted in apparatus precisely similar to that employed in the bleaching of cotton yarn, except in the operation of chemicking. Although steeping under sieve in dilute bleaching-powder solution might well be employed, it is usual to suspend the hanks of linen yarn on reels in such a manner that they are only partially immersed in the solution contained in a shallow tank. As the reels revolve the yarn becomes thus alternately impregnated with the solution and exposed to the air. The liberation of hypochlorous acid by the carbonic acid of the air is advantageous, and the bleach is more effective and regular.

The application of acetic acid, as proposed by Lunge, instead of this exposure to air, may here be strongly recommended, since then no insoluble lime salt is fixed on the fibre, and the subsequent souring could be reduced to a minimum.

To avoid the presence of caustic lime some bleachers use hypochlorite of magnesia, as proposed by Hodge, instead of bleaching powder.

**Linen-cloth bleaching.** The old method of bleaching linen-cloth consisted in alternately boiling the fabric with solutions of sodium carbonate and exposing on the grass, succeeded by souring, and rubbing with solutions of soap. The modern method, adapted from that employed for calico, is given in the following résumé. It is intended for 1,500 kilos. brown linen, using low-pressure kiers:—

1. *Lime-boil.* Boil 14 hours with 125 kilos. lime, 2,000 litres water; wash.

2. *Sour.* Steep 2-6 hours in dilute hydrochloric acid, sp.gr. 1.0025; wash in stocks, turn-hank, wash.
3. *Ley-boils.* First, boil 8-10 hours with 2,000 litres water containing resin-soap: 30 kilos. caustic soda (solid), 30 kilos. resin, previously boiled together with water; secondly, boil 6-7 hours with 2,000 litres water, 15 kilos. caustic soda (solid), previously dissolved; wash.
4. *Expose in field* 2-7 days according to the weather.
5. *Chemick.* Steep 4-6 hours in dilute bleaching - powder solution, sp.gr. 1.0025°; wash.
6. *Sour.* Steep 2-3 hours in dilute sulphuric acid, sp.gr. 1.005°; wash.
7. *Ley-boil (scald).* Boil 4-5 hours with 2,000 litres water, 8-13 kilos caustic soda (solid); wash.
8. *Expose in field* 2-4 days.
9. *Chemick.* Steep 3-5 hours in dilute bleaching - powder solution, sp.gr. 1.00125°; wash.

At this stage the cloth is examined; those pieces which are sufficiently bleached are soured and washed, the rest are further treated as follows:—

10. *Rub* with rubbing boards and a solution of soft soap.
11. *Expose in field* 2-4 days.
12. *Chemick.* Steep 2-4 hours in dilute bleaching - powder solution, sp.gr. 1.0006°; wash.
13. *Sour.* Steep 2-3 hours in dilute sulphuric acid, sp.gr. 1.005°.
14. Wash, squeeze, and dry.

If the linen is not brown, but made of yarn already partly bleached, the above process is much curtailed, and weaker liquors are employed.

The kiers, chemicking and souring machines are the same as those used in cotton yarn bleaching. The washing is done in the so-called wash-stocks or by slack-washing machines. The latter are very similar to the cotton-washing machines, the chief difference being that the water-tank is divided into compartments, each of which holds a few yards of slack cloth forming each strand before it passes through the squeezing rollers.

The 'rubbing' referred to, is for the purpose of removing mechanically any remaining brown particles of ligneous matter termed 'sprits.' It consists in passing the chain of cloth through a solution of soap, and then immediately between a pair of horizontal, corrugated, heavy boards; the upper board rests loosely upon the lower one, and moves lengthwise to and fro, while the pieces pass between them at right angles.

The operation of 'turn-hanking' consists in disentangling the pieces after they have been washed in the stocks, and then refolding them for a further wash, thus insuring a thorough cleansing of every portion of the cloth. When slack-washing machines are employed the operation is of course not necessary.

The chemistry of linen bleaching is essentially the same as that of bleaching cotton. The pectic acid, fatty matters, &c., are rendered soluble by the alkaline boilings, and the colouring-matters still remaining are oxidised and destroyed by hypochlorites. The repetition of these opera-



tions is considered necessary by reason of the large percentage of impurities present; but it is very probable that good results would be obtained by adopting the more rational plan of first removing the whole of the pectic and fatty matters before applying the hypochlorites. The steam-er process in conjunction with the application of acetic acid and hypochlorites is well worth the attention of practical linen bleachers.

**Wool scouring and bleaching.** The bleaching of wool never forms a separate industry, as in the case of cotton and linen, and although in itself of minor importance, it is necessarily preceded by the operation of 'scouring,' which is of fundamental importance both to the woollen manufacturer and the dyer.

In its natural condition the wool fibre is contaminated with 15-70 p.c. of foreign matter, consisting partly of dirt &c. derived from without, but mainly of certain fatty matters designated as 'yolk,' secreted by the animal from which it is derived. This secretion is separable into two parts: the one, 'wool-perspiration,' is soluble in water, and consists essentially of the potassium compounds of oleic and stearic acids (potash soaps) &c.; the other portion, termed 'wool-fat,' is insoluble in water, and is composed of cholesterine and iso-cholesterine, which exist partly in the free state, but chiefly in combination with oleic acid and other fatty acids.

**Loose-wool scouring.** The object of scouring wool is to remove from it the yolk, &c., and thus render it more suitable for spinning, dyeing, or bleaching. Two methods of effecting it may be employed. The one generally adopted is to treat

the wool with dilute alkaline solutions capable of forming emulsions with the yolk; the other mode is to submit the wool to the successive action of fat solvents, carbon disulphide, &c., and of water.

**Scouring with alkaline solutions.** When carried out in the most complete manner, as it is conducted in Belgium, this method comprises the following operations:

1. *Steep* several hours in tepid water.
2. *Scour* 15-30 minutes with dilute alkaline solutions (soap, sodium carbonate, &c.) at about 50°C.
3. *Wash* with water.

The *steeping* is performed in a series of large iron tanks, in which the wool is systematically washed or rather steeped in water heated to 45°C., until it is deprived of soluble matter. As a rule two to three steeps with fresh water are found sufficient; but it is customary to pass the wash water through several lots of wool until it becomes well saturated with 'wool-perspiration.' The operation is not carried out in England. It is particularly advantageous in the case of wools rich in yolk (*e.g.* Buenos Ayres wool, &c.), since it prevents too rapid soiling of the scouring bath and consequent staining of the wool, and thus it tends to ensure more complete scouring. By evaporating the waste steeping-liquors to dryness and calcining the residue, a good quality of potassium carbonate, containing very little sodium salts and suitable for glass manufacturers, is obtained.

The *scouring and washing* of the wool in order to remove the remaining 'wool-fat' is best

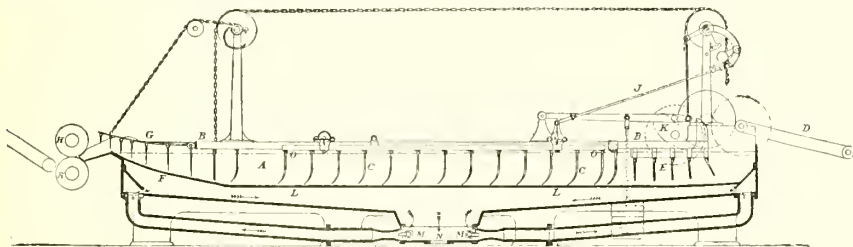


Fig. 9.

performed by the aid of so-called wool-scouring machines, one of which (J. & W. McNaught's) is shown in fig. 9.

It consists of a large rectangular trough A, with a light frame B suspended over it by chains and carrying a series of transverse, fixed, vertical rakes or combs C.

The wool, either in its raw condition or after steeping, is spread evenly on the moving endless apron or feeder D; it is thus continuously introduced at one end of the trough.

By suitable mechanism the frame is lowered, and the wool is at once pressed beneath the surface of the scouring liquor by the perforated tray or sieve E. When the frame is sufficiently lowered it moves forward, the rakes gently carrying the wool towards the other end of the trough. When the forward stroke is completed, the frame is lifted up, the rakes rise vertically out of the liquid, and the frame returns to its original position. By these successive movements the wool

is slowly passed through the scouring liquor. At the delivery end it is carried up the inclined plane F by the rakes fixed on the small frame G, which is hinged to the larger one. Having been pushed over the ridge, the wool slips down between the squeezing rollers H, ready to be passed through a second similar machine.

The working of the machine as above described is suitable for Botany and other fine classes of wool. When washing low Cape, River Plate, and similar wools which contain much dirt and sand, an additional movement is given to the rakes while in the liquor. This is effected by having the rakes fixed in a second frame O, which receives a slight backward and forward movement by means of the rod P and the cam Q, during the onward movement of the main frame R to which it is attached. By this means the wool is slightly opened out and agitated, and the sand and dirt fall through the perforated grating LL. When the scouring liquor becomes too

soiled for further use, the steam injectors *xx* are brought into action in order to stir up all sediment, and the dirty liquor is run off by the plug-hole *x*.

For a complete arrangement there should be at least three such machines placed in line, so that the wool passes automatically from one to the other. The first contains more or less soiled scouring liquid which has been previously used in the second trough; the second contains fresh scouring liquid, and the third a continual flow of clean, cold, or preferably tepid water.

The choice of scouring agent depends upon the character and quality of the wool. For fine lustrous wools and such as are poor in yolk, a mild scouring agent should be selected, *e.g.* soap, ammonia, ammonium carbonate, lant, &c., that is to say, agents which are capable of removing the yolk with the least injury to the fibre. The best soaps to use are those which are most soluble and least likely to contain any trace of caustic or carbonated potash or soda. Should these injurious constituents be present, the soap solution may be de-alkalised by the addition of a small quantity of boracic acid or ammonium chloride, thus yielding the less injurious alkali borates and ammonia, respectively.

Potash soaps being very apt to contain excess of alkali should be critically examined. An excellent and very soluble soap may be readily made from oleic acid and caustic soda.

Although a perfectly neutral soap does not always effect a rapid and complete removal of yolk, still it is better to adopt it, since one can always add the proper quantity of other agents, *e.g.* sodium carbonate, ammonia, &c., when necessary.

For low class wools containing a large proportion of yolk, and when cheapness is a desideratum, sufficiently satisfactory results are obtained by the proper use of sodium carbonate free from caustic soda or other injurious impurity. Suitable sodium carbonates are now sold under such commercial names as refined soda-ash, solvay soda, concentrated crystal soda (Brunner, Mond, & Co.), crystal carbonate (Gaskell, Deacon, & Co.), &c.

It is impossible to give precise data with respect to the concentration and temperature of the scouring solution to be employed, since these vary somewhat according to the character of the wool operated upon. If the best results are to be obtained the solutions must always be applied as dilute and at as low a temperature (about 50°C.) as is consistent with the complete removal of the yolk.

The waste scouring-liquors are collected in large tanks and neutralised with sulphuric acid; the liberated fatty acids are sold to oil refiners who by distillation obtain purer products, suitable for making soap.

**Scouring with volatile liquids.** This method is still only in an experimental stage, although it is probably the one which will be largely adopted in the future. Mechanical difficulties, the fear of fire and explosions, the first cost of the scouring agent, &c., seem to have prevented the general adoption of this process. Its advantages are that the wool-fat is more completely removed than by the emulsion method, and the wool itself is not injured. A certain

degree of success has been obtained by the method proposed in recent years by T. J. Mullings, and tried on a large scale. It consists in submitting the wool to the action of carbon disulphide in a closed centrifugal machine until the whole of the wool-fat is dissolved, then expelling the solvent by means of water, and not as heretofore by heat or steam, which always leaves the wool with a yellow colour. The wool must afterwards be washed in warm water to remove wool-perspiration and other impurities. The wool cleansed in this manner is said to be stronger, capable of spinning finer yarn and with less waste and at less cost than if scoured by the ordinary method with soap.

The same principle is adopted in the recently patented process of Singer and Judell of Adelaide, who employ, however, a more elaborate and more perfect apparatus, whereby the scouring is made continuous. The raw wool is placed on a feeding apron and carried along between two broad endless bands of wire gauze, first through a succession of fourteen tanks containing carbon disulphide and then through five containing water, all suitably inclosed. The wool, still held between the wire gauze bands, then passes between hot rollers in a steam-heated drying chamber and emerges in a scoured, washed, and dried condition. Arrangements for automatically collecting the dirt which settles from the carbon disulphide, for separating the latter from the water, distilling and returning it to the scouring tanks with the least possible loss, are all provided for by ingenious devices, and the general arrangement seems eminently typical of the method of scouring wool to be adopted in the future. It is said to have been already worked with success in Australia.

**Woollen-yarn scouring.** The object of scouring woollen yarn is to remove the oil with which wool has been impregnated by the spinner. Precisely the same agents are used as for loose wool, but the machinery employed is necessarily different.

Those yarns which have a tendency to curl up because they have been highly twisted are submitted to the preliminary operation of 'stretching'; it also prevents them from shrinking during the subsequent scouring process.

The hanks of yarn are suspended on the arms of a strong iron frame and tightly stretched by means of screws. Thus charged the frame is immersed in boiling water for a few minutes. After changing the position of the hanks on the arms, the operation is repeated, the yarn is allowed to cool in the stretched condition, and is then removed ready for scouring.

The scouring of yarn is effected either by hand or by machine. In the first case the hanks of yarn are suspended on wooden rods placed across a rectangular steam-heated tank containing the scouring liquor. During a period of fifteen to twenty minutes the rods are swayed to and fro by hand, one by one, each hank being frequently turned in order to expose every portion to the action of the liquor. The yarn is washed in another tank in the same manner.

Yarn-scouring machines are to be met with in several forms. A very effective one consists of a rectangular tank *c* having several rollers above and below, and a pair of squeezing rollers

A B situated at one end. The hanks of yarn, linked together by means of string loops, are passed continuously through the scouring liquor, and are then washed in a similar machine (see fig. 10).

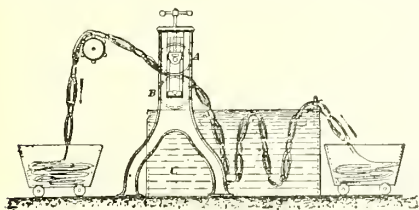


FIG. 10.

**Woollen-cloth scouring.** Woollen cloth is also scoured for the purpose of removing the oil with which the yarn is impregnated by the spinner. The operation consists in passing the cloth as an endless band, either in the chain form or in the open width, through the scouring liquor and then through a pair of squeezing rollers.

For thick woollen cloths, flannels, &c., the chain-scouring is preferred, since a certain amount of felting takes place and the cloth acquires a better handle. For worsted goods and such as are liable to crease, scouring in the open width is preferable.

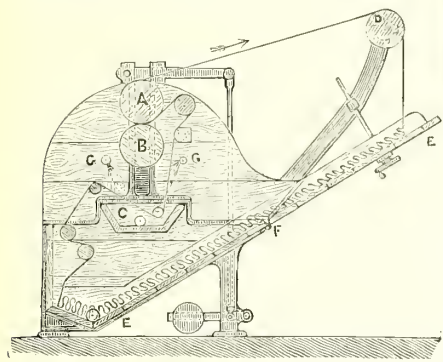


FIG. 11.

Figure 11 shows a section of E. Kempe's machine for this purpose. It consists of two squeezing rollers, A and B, placed above the wooden trough C containing the scouring liquor. The roller D serves to draw the cloth from the squeezing rollers, and causes it to fall in regular folds upon the inclined plane DE. This is covered with corrugated zinc, the grooves of which run longitudinally, in order to reduce the friction of the cloth, and to prevent the latter from moving to either side. The upper part of the inclined plane is hinged at F so that the inclination of this part can be regulated to suit different qualities of cloth, and to ensure that it always slips down in regular folds without any tendency to fall over or become blocked. The perforated water-pipes GG are for the purpose of washing the cloth after scouring.

**Bleaching of wool.** After scouring, the wool still possesses a faint yellow tint, to re-

move which is the object of the bleaching proper. The agent almost universally employed is sulphur dioxide, either in the form of gas (gas-bleaching) or in solution (liquid-bleaching). Hydrogen dioxide is still too expensive to admit of extended application, but it serves as an excellent bleaching agent for certain fine materials.

**Gas-bleaching, stoving, or sulphuring,** consists in exposing the scoured and washed woollen material, while still wet, to the action of sulphur dioxide in a brick chamber. Yarn or thick cloth is suspended on poles, the sulphur (6-8 p.c. on the weight of wool) contained in an iron pot is ignited, the chamber door is closed, and the material is then left exposed to the action of the gas for six or eight hours, or even overnight. Thin cloth is generally passed in a continuous manner through a similar chamber provided with rollers above and below. The cloth in the open width enters through a narrow slit at one end of the chamber; it passes in a zig-zag course under and over the rollers to the further end, then returns and passes out by the same slit. The sulphur dioxide is prepared in the stove itself, or it is produced in a separate furnace and led beneath the perforated floor of the chamber. According to the appearance of the fabric it is passed through the bleaching chamber one or more times. Fig. 12 gives a sectional view of the sulphur stove for the continuous bleaching of cloth.

In *liquid-bleaching* the woollen material is immersed and moved about for several hours in a solution of sulphurous acid, or in one containing sodium bisulphite, and acidified with sulphuric acid. One may also steep the wool, first in a solution of sodium bisulphite and then in dilute sulphuric acid, and repeat the operations as often as may be necessary. The liquid-bleaching process has not met with that general acceptance to which it seems entitled.

After bleaching, the materials are well washed and tinted blue or bluish-violet, *e.g.* with refined indigo, indigo-extract, aniline-blue, &c. in order to counteract the yellowish tint which is so liable to return. Blue and yellow, as complementary colours, tend to produce white.

The bleaching action of sulphurous acid is most probably due to its reducing properties. According to this view the sulphurous acid takes up oxygen from the water present, while the liberated hydrogen combines with the colouring matter of the wool to form a colourless hydrogen compound. Another explanation, however, is that a colourless sulphite compound may be formed. Frequent washing of the wool with alkaline solutions restores the yellow colour, either by effecting oxidation of the colourless hydrogen compound, or by decomposing the sulphite compound and precipitating the original yellow colouring matter. It seems evident, however, that the yellowing influence of alkalis is largely due to their further action upon the wool substance itself, since they cause the wool eventually to become yellower than it was before bleaching.

Bleaching with hydrogen peroxide is effected by steeping the wool for several hours in more or less dilute solutions of this liquid made slightly alkaline by the addition of ammonia. The simultaneous action of light accelerates and



improves the bleaching. The white is very good and permanent, probably because in this case, the colouring matter is destroyed by oxidation. Excessive bleaching by this method gives the wool a harsh feel. Lunge recommends a slight treatment with hydrogen peroxide of sulphur bleached wool in order to oxidise and thus render innocuous traces of sulphurous acid not removed by washing. A very dilute solution of sodium hypochlorite and exposure to air will effect the same purpose.

**Silk scouring and bleaching.** The raw silk fibre consists essentially of two substances, *fibroin* and *sericin*. The former constitutes the central portion of the fibre and may be regarded as the fibre proper, while the latter resides principally in the external part and is readily re-

moved by water and especially alkaline solutions.

Raw silk is harsh, stiff, lustreless, and more or less unsuitable for dyeing, but when the external *sericin* or silk-glue is removed it becomes soft and lustrous, and acquires an increased affinity for colouring matters.

The object then of scouring is to remove the silk-glue from the raw silk. It is effected by the two operations, '*stripping*' and '*boiling-off*.'

**Stripping or ungumming.** In order to remove calcareous or other mineral matter soluble in dilute acids, it is well first to rinse the silk in a tepid bath of dilute hydrochloric acid, and then wash. The hanks of silk are then hung on smooth wooden rods and worked, as in woollen-yarn scouring, in a soap bath heated to about

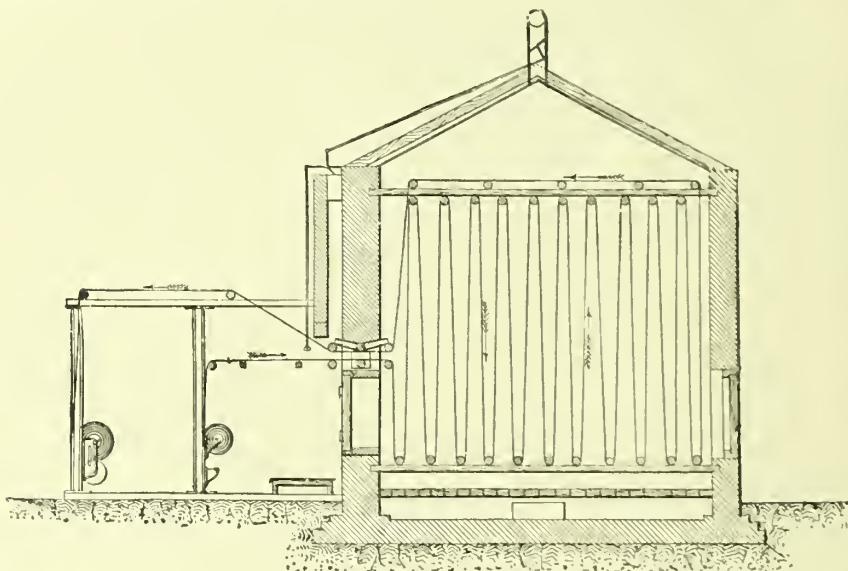


FIG. 12.

90°-95°C. for about twenty minutes. A second, and even a third bath may be used with advantage. Long working in one bath is not good, especially for silk intended to be white, since the silk (*fibroin*) is apt to attract some of the colouring matter at first removed along with the silk glue, and it is afterwards very difficult to remove. With yellow silk this point must be carefully attended to.

During the stripping operation the *sericin* at first swells up and makes the silk somewhat glutinous, but soon it dissolves off and leaves the fibre soft and lustrous. The waste soapy liquors, strongly impregnated with *sericin*, are carefully preserved and find an important use in silk-dyeing under the name of '*boiled-off liquor*.' When applying the coal-tar colours, it serves to retard their attraction by the silk and thus ensures the production of even or level colours.

After stripping the silk is rinsed in water containing a small proportion of soap and sodium carbonate.

**Boiling-off.** The object of this operation is to complete the removal of the silk-glue and

thus give the silk all the lustre and brilliancy of which it is capable. The hanks of silk are tied up in coarse bags of cotton or hemp, generally called '*pockets*,' and these are boiled for one to three hours in open copper boilers. The silk is then well rinsed in a weak tepid solution of carbonate of soda, and finally in cold water.

During the operations above described, Japanese and Chinese silks lose 18-22 p.c. in weight, European silks lose 25-30 p.c.

**Bleaching of silk.** The actual bleaching of silk is effected by exposing the scoured silk while still in the wet state to the action of sulphur-dioxide gas. The operation is precisely similar to the stoving of wool.

In certain cases, *e.g.* with so-called '*souple*' silk, the stoving is preceded by a preliminary bleaching in aqua regia, diluted to sp.gr. 1.02 and heated to 20°-35°C. The silk is rinsed in this solution for 8-15 minutes until it acquires a greenish-grey colour, and then at once washed well in cold water. A dilute solution of the so-called '*chamber-crystals*' of the sulphuric acid manufacture may replace the aqua regia.

The bleaching of silk with hydrogen peroxide is gradually being more and more adopted, especially for Tussur silk and other wild silks. Indeed for these silks no other method of bleaching is so satisfactory. The silk is steeped and worked in a dilute solution of hydrogen peroxide, rendered slightly alkaline with ammonia, until it is sufficiently bleached. A more rapid and effective method is to steep the silk in a somewhat stronger solution, then wring out the excess of liquid and steam. The operations may be repeated until the silk is sufficiently bleached.

**Tinting of silk.** Bleached silk is finally tinted or dyed in delicate shades of blue, purplish-blue, cream colour, &c. For pure white it is usual to dye the silk in a very dilute solution of ammoniacal-cochineal and indigo-carmin. Various suitable coal-tar colours are also employed. After tinting, the silk is slightly rinsed in water and dried in a moderately warm and darkened stove. J. J. H.

**BLLENDE**, from *Blenden*, Ger., to dazzle. Native zinc sulphide. It usually contains iron sulphide which gives it a black colour, whence the name Black Jack applied to it. An important ore of zinc. The sulphur it contains is occasionally utilised in the manufacture of sulphuric acid. For descriptions of burners for this purpose v. S. C. I. 3, 631; 4, 54.

**BLEU DIRECT** or **DIPHENLYAMINE BLUE** v. **TRIPHENYLMETHANE COLOURING MATTERS**.

**BLEU FLUORESCENT**  $C_{15}H_{11}Br_2N_3O(NH_4)$ . A colouring matter obtained by Weselsky and Benedikt in 1880 by treating diazoresorufin dissolved in potassium carbonate with bromine and precipitating by an acid. Soluble in boiling water with a red-violet colour, giving a fluorescent green solution. Dyes silk and wool blue with brownish fluorescence (Weselsky and Benedikt, M. 5, 605; B. 1885, 18; Ref. 26).

**BLEU DE GARANCE.** Artificial ultramarine, v. **ULTRAMARINE**; **PIGMENTS**.

**BLEU LUMIERE** v. **TRIPHENYLMETHANE COLOURING MATTERS**.

**BLEU DE LYON, BLEU DE NUIT, BLEU DE PARIS** v. **TRIPHENYLMETHANE COLOURING MATTERS**.

**BLEU MARIN** v. **TRIPHENYLMETHANE COLOURING MATTERS**.

**BLEU DE SAXE** v. **COBALT**.

**BLEU SOLUBLE** v. **TRIPHENYLMETHANE COLOURING MATTERS**.

**BLIND-COAL.** A Scotch term for anthracite.

**BLISTER STEEL** v. **IRON**.

**BLOCK FUEL** v. **FUEL**; also **PITCH**.

**BLOCK TIN** v. **TIN**.

**BLOOD** is the general circulating fluid of animals indispensable to the nourishment and growth of their bodies, and from it the raw materials for their secretions are obtained by the secretory glands. In the mammalia, in birds, and the tunny fish the blood is warm, and varies in appearance according to the vessels in which it is found; in the arteries it is brilliant scarlet, but in the veins it is of a dark purplish tint, the main difference, from a chemical point of view, being the fact that the venous blood holds carbonic acid in solution (probably in combination with the sodium present), which is removed in the lungs, while in the arteries free

oxygen is present. In the invertebrata the blood is cold and (with numerous exceptions) colourless.

Mammalian blood consists of plasma, a transparent nearly colourless fluid in which are contained a number of red corpuscles and a few white corpuscles. The percentage of red (and white) corpuscles is widely variable in different members of the vertebrate series, and in the same the red corpuscles always carry the colouring matter. In many invertebrates, however, the latter is diffused throughout the plasma. For particulars of the composition of mammalian blood see M. Foster's *Text Book of Physiology* and A. Gamgee's *Physiological Chemistry of the Animal Body*. Fresh blood has an alkaline reaction and a saline and somewhat sweetish taste.

Blood is used in the clarification of wines and syrups; in the preparation of adhesive cements; in the manufacture of pure animal charcoal; as a precipitant of sewage in the 'alum, blood and clay' process, and as a source of albumen (*q. v.*). Blood may be prepared as an article of food by heating defibrinated ox blood on a steam bath for 4 or 5 hours, and then finally drying at a temperature of from 40°-45°C. in a stream of air, a process taking about 3 days, when it forms a dry friable powder (Guerder, Ph. Centralb. 1883, 385). H. P. Madsen has patented (Eng. Pat. 10,995, Aug. 28, 1886) a process in which the blood is mixed with salt and saltpetre, filtered and then dried. G. le Bon (C. R. 81, 526) claims to have obtained dried blood in a perfectly soluble form by evaporating it at the temperature of the body, but he does not give details of his method.

The utilisation of blood as manure has attracted considerable attention. Vantelet (C. R. 90, 1,365) preserves blood for agricultural purposes by adding in proper proportions aluminium sulphate, sulphuric and nitric acids. Delacharlonny (C. R. 95, 841) obtains a solid manure by adding to the blood an acid ferric sulphate of the composition  $Fe_2O_3.4SO_4.12H_2O$ , instead of the neutral sulphate, obtaining thereby a coagulum at ordinary temperatures which loses half its water by drainage, whilst the remainder can be easily expressed by pressure, the resulting mass being allowed to dry under cover. The acid sulphate can be readily prepared by adding nitric acid to ferrous sulphate, to which sufficient sulphuric acid has already been added. On concentrating the solution the salt crystallises out. A solution in water of 45° B. is prepared, and a litre of blood requires 45 c.c. of this solution for complete coagulation. Strype (Eng. Pat. 787, 1884) prepares a manure by adding a solution of iron sulphate, alum, &c. to blood. Müller (Landw. Versuchs. 32, 302) prepares a manure by mixing the blood with peat and chalk, and v. Stein (Ger. Pat. 36,094, 1885) mixes together blood, alkaline phosphates, carbonates, nitrates, sulphates, silicates, and dextrine, and subsequently dries and grinds the mixture.

As regards the efficacy of blood as a manure, see Eckenbrecher (Landw. Versuchs. 31, 165), Petermann (Ann. Agronomiques, 9, 241) finds the action on a loam to be nearly as beneficial as that of sodium nitrate. Richter has patented (Ger. Pat. 13,594, 1880) a process for obtaining

ammonia from blood by treating it with caustic potash, drying and distilling.

Johnson prepares blood as a medium for painting by either removing the fibrine and adding one-tenth its bulk of a solution of an alkaline silicate, or else by adding sufficient caustic alkali to dissolve the fibrine. He then reduces its consistency with water so that when mixed with paint or pigments it will work properly under the brush (Eng. Pat. 82, 1883).

**BLOODSTONE.** A hard compact variety of hæmatite used for burnishing gilt coat buttons and the gold on china.

**BLOOM.** A term given to a mass of iron after it leaves the puddling furnace (v. Iron).

**BLOOMERY.** An old term for an iron furnace.

**BLOWPIPE** v. ANALYSIS.

**BLUE, ACETIN,** *Coupler's blue*, v. INDULINES.

**BLUE, ALIZARIN.** This name is given to dioxyanthraquinone-quinoline  $C_{11}H_9NO_4$ , and its sodium bisulphite compound  $C_{17}H_{11}NO_{10}S_2Na_2$

(v. ALIZARIN AND ALLIED COLOURING MATTERS).

**BLUE, ALKALI, NICHOLSON'S BLUE** or **SOLUBLE BLUE**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, ANILINE, GENTIAN BLUE, OPAL BLUE, NIGHT BLUE, LIGHT BLUE, or FINE BLUE**, v. TRIPHENYLMETHANE COLOURING MATTERS. Also ANILINE BLUE.

**BLUE, ANTWERP**, v. PIGMENTS.

**BLUE, AZO**, v. AZO-COLOURING MATTERS.

**BLUE, AZODIPHENYL, ACETIN BLUE, COUPIER'S BLUE, INDULIN, FAST BLUE R.**  $C_{18}H_{15}N_3Cl$ , v. INDULINES.

**BLUE, BASLE, tolyldimethylamidophenotolylimidonaphthazonium chloride**  $C_{32}H_{29}N_4Cl$ , v. AZINES AND COLOURING MATTERS DERIVED FROM THEM.

**BLUE, BAVARIAN** v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, BENZIDINE**, v. AZO-COLOURING MATTERS.

**BLUE, BLACKLEY**, v. INDULINES.

**BLUE, BRILLIANT COTTON, METHYL BLUE, METHYL WATER BLUE.** Soda salt of triphenyl- $\beta$ -rosaniline-trisulphonic acid, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, CERULEAN**, v. PIGMENTS.

**BLUE, CHINA, WATER BLUE 6 B EXTRA, OPAL BLUE, COTTON BLUE, MARINE BLUE**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, CHINESE, or PRUSSIAN BLUE**, v. CYANIDES; also PIGMENTS.

**BLUE, COBALT**, v. COBALT; also PIGMENTS.

**BLUE, COTTON**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, COUPIER'S**, v. INDULINES.

**BLUE, CYANINE**, v. PIGMENTS.

**BLUE, DIPHENYLAMINE, BLEU DIRECT** triphenyl  $\beta$ -rosaniline hydrochloride (?), v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE-ETHYLENE** v. THIONINE COLOURING MATTERS.

**BLUE, FAST, MELDOLA'S BLUE, NEW BLUE, NAPHTHYLENE BLUE.** Chloride of dimethylphenyl-ammonium- $\beta$ -naphthoxazin, v. OXAZINE COLOURING MATTERS.

**BLUE, FLUORESCENT**, v. BLEU FLUORESCENT.

**BLUE, GENTIAN, SPIRIT BLUE O. OPAL BLUE, BLEU DE NUIT, BLEU LUMIÈRE, FINE BLUE**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, INDIAN**, v. PIGMENTS.

**BLUE, INTENSE**, v. PIGMENTS.

**BLUE, LEITCH'S**, v. PIGMENTS.

**BLUE, LIGHT, BLEU LUMIÈRE, OPAL BLUE, BLEU DE NUIT**, v. TRIPHENYLMETHANE COLOURING MATTERS.

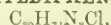
**BLUE, LYONS, BLEU LUMIÈRE, OPAL BLUE, &c.**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, MARINE**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, MELDOLA'S**, v. OXAZINE COLOURING MATTERS.

**BLUE, METHYL**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, METHYLDIPHENYLAMINE,**



obtained in 1874 by Girard by the action of oxalic acid upon methyldiphenylamine. Or by the action of copper nitrate (Bardy and Dusart). Or with chloranil (Geigy). No longer made.

**BLUE, METHYLENE**, v. THIONINE COLOURING MATTERS.

**BLUE, NAPHTHYLENE, NEW BLUE, FAST BLUE, MELDOLA'S BLUE**, v. OXAZINE COLOURING MATTERS.

**BLUE, NEUTRAL**, v. AZINES AND COLOURING MATTERS DERIVED FROM THEM.

**BLUE, NEW**, v. OXAZINE COLOURING MATTERS.

**BLUE, NICHOLSON'S, ALKALI BLUE, SOLUBLE ANILINE BLUE**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, NIGHT**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, NILE**, v. OXAZINE COLOURING MATTERS.

**BLUE, OPAL**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, PARIS**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, PRUSSIAN**, v. CYANIDES; also PIGMENTS.

**BLUE, QUINOLINE**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, RESORCIN, or LACMOID**  $C_{12}H_8NO_2$ ?

probably  $N \left\{ \begin{array}{l} C_6H_3(OH)_2 \\ C_6H_2 \begin{array}{l} \text{OH} \\ \text{O} \end{array} \end{array} \right.$ , a colouring matter ob-

tained by Benedikt and Julius in 1884, by the action of sodium nitrito on resorcin. Blue violet powder soluble in water. Soluble in alcohol with blue colour and dark green fluorescence. Used as an indicator in alkalimetry.

**BLUE, SAXON**, v. COBALT.

**BLUE, SOLUBLE ANILINE, NICHOLSON'S or ALKALI BLUE** v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, SPIRIT, OPAL BLUE, BLEU DE NUIT, BLEU LUMIÈRE**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, VICTORIA**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE, WATER, OPAL BLUE, CHINA BLUE, BLEU MARIN**, v. TRIPHENYLMETHANE COLOURING MATTERS.

**BLUE BLACK, or AZO-BLACK**, v. AZO-COLOURING MATTERS.



**BLUE COPPERAS, BLUE STONE, or BLUE VITRIOL.** *Copper sulphate*, *v.* COPPER.

**BLUE GUM TREE.** The *Eucalyptus globulus*, a tree common in Tasmania and South-Eastern Australia.

**BLUE IRON-EARTH or ORE.** *Vivianite*. Hydrated triferrous phosphate, or ferroso-ferrie phosphate, occurs native in North America, Russia, &c., in monoclinic crystals or in reniform globular masses. Colourless, changing to blue or green on exposure to air. An incrustation of vivianite is occasionally met with on bones buried in ferruginous soils.

**BLUE JOHN.** A variety of fluorspar found in Derbyshire, and valued for making ornamental articles (*v.* CALCUM).

**BLUE LEAD.** A term applied to galena by miners to distinguish it from white-lead ore, or carbonate.

**BLUE PIGMENTS** *v.* PIGMENTS.

**BODY VARNISH** *v.* VARNISH.

**BOG BUTTER.** Adipocere found in bogs (*v.* ADIPOCERE).

**BOGHEAD COAL** *v.* PARAFFIN.

**BOGHEAD NAPHTHA** *v.* PARAFFIN.

**BOG IRON ORE** *v.* IRON, ORES OF.

**BOG MANGANESE, wad,** or earthy manganese, *v.* MANGANESE.

**BOHEMIAN BOLE.** A yellow variety of bole (*q. v.*).

**BOILED OIL.** Linseed oil boiled with litharge, to render the oil more 'drying,' that is, to cause it to solidify more readily.

**BOIS-PIQUANT BARK.** The bark of *Xanthoxylon caribaeum*, and *X. Perrottetii*. Used in France as a febrifuge (Heckel *o.* Schilgdenhaffen, C. R. 98, 996, Ph. [3] 14, 965).

**BOLDO.** A shrub (*Boldoa fragrans*) belonging to the *Monimiaceae*, growing in the Chilean Andes. The bark is used in tanning, the wood makes a good charcoal, and the bark and leaves contain a glucoside  $C_{20}H_{32}O_{13}$ , useful as a hypnotic and cholagogue (Chapoteau, C. R. 98, 1,052; C. J. [2] 46, 845).

**BOLE.** (*Bol*, Ger.) A ferruginous clay-like substance, of red, brown, or yellowish colour. It is not plastic, and when thrown into water falls to pieces with emission of streams of minute air-bubbles. It has an unctuous feel, and some varieties adhere to the tongue. When cut it presents a shining streak. Before the blowpipe it fuses to a yellowish or white enamel. Its composition is very variable, but its usual limits are from 41 to 47 p.c.  $SiO_2$ , 18 to 25 p.c.  $Al_2O_3$ , and 24 to 25 p.c.  $H_2O$ , with a proportion of  $Fe_2O_3$  which may reach 12 p.c. It will be noticed that the percentage of water is higher than in clays. The *Fettbol* of Freiberg in Saxony occurs in mineral veins, and contains only about 3 p.c. of  $Al_2O_3$ . The bole of Stolpen in Saxony is a yellowish substance containing only a trace of  $Fe_2O_3$ . Rammelsberg's analysis yielded  $SiO_2$ , 45.92;  $Al_2O_3$ , 22.14;  $CaO$ , 3.9;  $H_2O$ , 25.86. In the bole of Sinope the  $SiO_2$  falls as low as 32 p.c. The ancients obtained this material from Cappadocia, and used it as a red pigment. It was also employed in medicine as an astringent (*v.* LEMNIAN EARTH).

The following is an analysis of bole, occurring in granite, at Steinkirchen, Bohemia. Dried at 100°C. it yielded  $SiO_2$ , 46.734;  $Al_2O_3$ ,

26.166;  $Fe_2O_3$ , 12.345;  $CaO$ , 1.641;  $MgO$ , 1.315;  $K_2O$ , 0.978;  $MnO$ , 0.280; loss on ignition, 10.53 (G. Starkl, Verh. k. k. Geolog. Reichs., Vienna, 1880, 279).

Bole is frequently found as a product of the decomposition of basaltic rocks. Thus the sheets of dolerite in NE. Ireland, representing tertiary lava-flows, are separated by partings of bole, associated with lithomarge, bauxite, pisolitic iron-ore, and seams of lignite. The Antrim bole is described as a poor variety of aluminous iron-ore (Tate and Holden, Quart. Journ. Geol. Soc., 26, 1870, 155; G. H. Kinahan, Journ. R. Geol. Soc. Ireland, 16, 1886, 306; P. Argall, *ibid.* 98).

F. W. R.

**BOLOGNIAN PHOSPHORUS** *v.* BARIUM.

**BOLOGNIAN STONE.** A native variety of barium sulphate, which is phosphorescent when partially reduced to sulphide by calcination with charcoal (*v.* BARIUM).

**BOLORETIN** *v.* RESINS.

**BONE.** Bone tissue may be either *compact* as in the shafts of the long bones of the extremities, or *spongy*, as in the flat bones of the skull or extremities of the long bones, each of which consists of an external compact layer, inclosing a mass of *spongy* tissue. Bone usually has a laminated structure, the layers being concentric with the tubes and channels containing the marrow or nutritive blood vessels. Its organic structure can be readily demonstrated by immersing a section in dilute hydrochloric acid. It consists of a matrix (which is mostly composed of so-called bone-cartilage [ossein]), which is in life impregnated with inorganic matter, mainly composed of tricalcic phosphate. On treating a bone, freed from fat by extraction with ether, with dilute hydrochloric acid, the structure, whilst retaining its form, loses its rigidity and becomes translucent, and on boiling with water forms glue (*q. v.*). Bone cartilage has the same composition as gelatin.

	C	H	N	O+S	
Isinglass	50.76	6.64	18.32	24.69	Mulder
Cartilage	50.40	6.64	18.34	24.64	Mulder
" from fossil bones	50.40	7.11	18.15	24.34	v. Bibra

The amount of S is about 0.216 p.c. (*v.* Bibra).

The cartilage of fetal bones does not appear to be convertible into gelatin (glue) by long-continued boiling (Schwan; Hoppel).

On heating out of contact with air, bones evolve a large quantity of volatile matter (*v.* BONE OIL) and leave a black residue, consisting of the inorganic matter associated with carbon, constituting animal charcoal (*q. v.*). In presence of air the ignited bone leaves a white residue of calcium and magnesium phosphates, with more or less free lime and carbonic acid, and small quantities of fluorine forming bone-ash. Iron and chlorine do not appear to be normal constituents of bone.

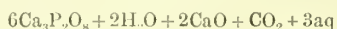
The quantity of fat and water in bone appears to vary within comparatively wide limits, being dependent on the nature of the bone and the health of the individual. The proportion of ash to cartilage is, however, fairly constant within certain limits. It appears from the observations of Fremy and v. Bibra

that the proportion of inorganic matter is smaller in youth than in age, and greater in compact bones than in spongy bones; greater also in the bones of the extremities than in those of the trunk, greatest of all in the thigh-bone. It appears, indeed, to be greatest in those bones which have to bear the greatest strain. The bones of mammals have the same average composition, although the bones of herbivorous quadrupeds generally contain a larger proportion of lime salts than those of flesh-eaters. Fish bones exhibit the greatest variety of composition; some are nearly pure cartilage, whilst others have the same proportion of organic and inorganic matter as those of mammiferous animals.

The general nature of bone-ash may be seen from the following analyses (Heintz):—

	Ca	PO <sub>5</sub>	CO <sub>2</sub>	F	Mg
Human	38.59	53.75	5.44	1.74	0.48
Sheep	38.52	53.29	5.65	1.97	0.58
Ox	38.52	52.98	6.04	1.89	0.57

The manner in which the inorganic constituents of bone are associated together is not definitely settled. It is usually supposed that the phosphoric acid and fluorine are combined with calcium to form a body resembling apatite, which is intimately mixed with calcium carbonate. Alby, however, regards normal bone-ash as having the composition



(J. pr. [2] 5, 308, *et seq.*).

Experiments with pigeons have shown that no alteration in the proportion of inorganic to organic substances, or of lime to phosphoric acid, is brought about by increasing the proportion of lime or phosphoric acid in the food. For further information on the influence of food on the composition of bone *v. Roloff*, Arch. f. wiss. Thierchik. 1, 189, 3, 152; Heitzmann, J. f. Thierchem. 1873, 229; Forster, Zeit. f. Biol. 12, 464; Lehmann, J. f. Thierchem. 1878, 272; Voit, Zeit. f. Biol. 16, 55; Weiske, Zeit. f. Biol. 7, 179, and 333; Weiske and Wildt, Zeit. f. Biol. 9, 541; Heiss, Zeit. f. Biol. 12, 151.

**BONE BLACK** *v.* ANIMAL CHARCOAL.

**BONE EARTH.** The calcined residue of bones. Consists chiefly of calcium phosphate (*v. Bone*).

**BONE OIL.** *Animal oil; Dippel's oil; Oil of hartshorn; Oleum animale empyreumaticum; Oleum cornu cervi; Oleum Dippelii.* (Ger. Knochenöl, Thieröl.) The product obtained by distilling bones in the preparation of bone black or animal charcoal.

The bones are first boiled in a large quantity of water, which removes the greater part of the fatty matters; they are then roughly dried and are subjected to dry distillation in iron retorts, similar to those used in the manufacture of coal gas. Bone black or animal charcoal remains behind and bone oil distils. The products of distillation are conducted through long iron tubes, which act as condensers and lead into receivers where the crude bone oil collects, together with water. The gases are then passed into a separator containing sulphuric acid to retain ammonia, and can afterwards be used for heating purposes, or, if passed through purifiers, for illumination.

The crude oil is separated from the aqueous distillate and is subjected to redistillation. The aqueous liquid consists of a solution of ammonium sulphide, ammonium thiocyanate and cyanide, ammonium carbonate, and small quantities of very volatile organic bases. This is treated with sulphuric acid and afterwards distilled with slaked lime. The distillate on treating with solid potash yields large quantities of ammonia, whilst some oily bases separate out, and are afterwards worked up with the bases contained in the crude oil. This latter is a dark-brown, nearly black liquid, having a fetid, most offensive smell and a sp.gr. .970.

On subjecting it to redistillation it begins to boil at 80°, when quantities of ammonia come over together with an oil. The thermometer rises very gradually to about 250°. From 180° upwards large quantities of ammonium cyanide and ammonium carbonate sublime over, and care has to be taken to prevent the condenser being stopped up. A black resinous tar remains, which is employed in making Brunswick black.

The following substances have been isolated from bone oil by fractional distillation combined with treatment with acids to separate basic from non-basic constituents:—

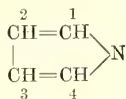
Chief constituents	Subsidiary constituents
Butyro-nitrile	Methylamine
Valero-nitrile	Ethylamine
Hexo-nitrile	Aniline
Isohexo-nitrile	Pyridine
Deco-nitrile	Methyl-pyridine
Palmito-nitrile	Dimethyl-pyridine
Stearo-nitrile	Quinoline
Pyrrol	Phenol
Methyl-pyrrol	Propionitrile
Dimethyl-pyrrol	Valeramide
Hydrocarbons	Toluene
	Ethyl-benzene
	Naphthalene

(Weidel and Ciaucian, B. 13, 65).

As to the formation of the various compounds in bone oil, the nitriles are formed by the action of ammonia on the fatty acids, pyrrol and the pyrrols are the products of decomposition of the gelatinous substances, and pyridine and its derivatives are condensation products of acrolein, from the dry distillation of the fats, with ammonia, methylamine, &c.

**Pyrrol.** That portion of the non-basic part of bone oil boiling at 98–150° contains pyrrol and its homologues. That above 150° contains dimethylpyrrol. The fraction 140–150° consists of a mixture of homopyrrols — *i.e.* methylpyrrols. To separate the  $\alpha$ - and  $\beta$ -derivatives, the mixture is converted into the potassium compound and heated in a current of carbon dioxide to 200°. Two isomeric homopyrrol carboxylic acids are formed, which differ in the solubility of their lead salts.  $\alpha$ -Homopyrrol carboxylic acid melts at 169.5°, and its lead salt is very soluble in water, differing from the  $\beta$ -acid, which melts at 142.4° and forms a slightly soluble lead salt. The acids obtained respectively yield on distillation with lime the corresponding methylpyrrols.  $\alpha$ -Homopyrrol boils at 148° under 750 mm. pressure, and  $\beta$ -homopyrrol at 143° at 743 mm.

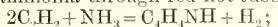
The constitution of pyrrol is represented as follows:



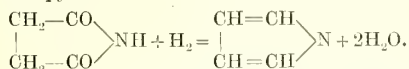
the positions 1 and 4 and 2 and 3 being known as the  $\alpha$ - and  $\beta$ - positions respectively. It boils at  $130$ – $131^\circ$ , and its sp.gr. is .9752 at  $12^\circ$ . It is slightly soluble in water, readily soluble in alcohol and ether. It is a weak base, and is only slowly dissolved by dilute acids in the cold. On heating with acids it is converted into an amorphous brown powder known as pyrrol-red, the reaction occurring according to the equation  $3\text{C}_4\text{H}_5\text{N} + \text{H}_2\text{O} = \text{C}_{12}\text{H}_{11}\text{N}_3\text{O} + \text{NH}_3$ .

Pyrrol forms colouring-matters with isatine, quinone, and phenanthraquinone (Meyer and Stadler, B. 17, 1,034). By the action of iodine on potassium pyrrol, tetriodopyrrol is formed, which crystallises in yellowish-brown prisms and decomposes at about  $140^\circ$ . It acts like iodoform as an antiseptic, and is known as iodo. It has the advantage over iodoform of being free from smell.

Pyrrol has been synthesised by passing acetylene and ammonia through red-hot tubes:



also by distilling the ammonium salts of mucic and saccharic acids. Succinimide, on heating with zinc-dust containing zinc hydrate, also yields pyrrol:



Potassium dissolves in pyrrol with the formation of potassium pyrrol  $\text{C}_4\text{H}_5\text{NK}$ , a substance insoluble in ether and decomposed by water into pyrrol and potassium hydroxide. This substance reacts with alkyl iodides to form substituted pyrrols—e.g.:

Methylpyrrol  $\text{C}_4\text{H}_4\text{NCH}_3$ : boils at  $113^\circ$ ; sp.gr. .9203.

Ethylpyrrol  $\text{C}_4\text{H}_4\text{NC}_2\text{H}_5$ : boils at  $131^\circ$ ; sp.gr. .9042.

Phenylpyrrol  $\text{C}_4\text{H}_4\text{NC}_6\text{H}_5$ , obtained by distilling the anilides of mucic and saccharic acids, melts at  $62^\circ$ . The homologues of pyrrol contained in bone oil are, however, all substituted in the group  $\text{C}_4\text{H}_4$ .

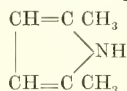
By the action of benzalchloride on pyrrol in presence of sodium a phenylpyridine is obtained in which the phenyl is in the meta- position to the nitrogen (Ciamician and Silber, B. 20, 191).

Nascent hydrogen converts pyrrol into pyrroline  $\text{C}_4\text{H}_5\text{NH}$ , a liquid boiling at  $91^\circ$  which dissolves easily in water. It yields, with nitrous acid, a nitrosoamine  $\text{C}_4\text{H}_5\text{N.NO}$ , m.p.  $37^\circ$ , and on heating with methyl iodide gives methylpyrrol (B. 16, 1,536).

Pyrrol reacts with diazo-compounds with the formation in an acid solution of an azo-compound, and in a neutral or alkaline solution of a disazo-compound, or a mixture of this with an azo-compound (Fischer and Hepp, B. 19, 2,251).

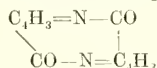
Numerous syntheses of pyrrol derivatives have been effected by Paal (B. 19, 558; 19, 3,156) from acetonylacetone by the action of ammonia and amines.

The dimethylpyrrol contained in the fraction of bone oil boiling above  $150^\circ$  has been obtained synthetically as follows: By the action of ammonia on diacetosuccinic ether, the ether of dimethylpyrrol dicarboxylic acid is obtained. This, on saponification, yields the acid, and, on heating, carbon dioxide is split off, leaving dimethylpyrrol. It has the composition



and is an almost colourless oil boiling at  $165^\circ$ . It is very volatile with steam, colours a pine splint an intense red, and yields on boiling with acids a pyrrol-red similar to other pyrrol homologues.

**Pyrrolcarboxylic acids**  $\text{C}_4(\text{NH})\text{H}_3\text{CO}_2\text{H}$ . The  $\alpha$ -acid is obtained from  $\alpha$ -homo-pyrrol by fusion with potash or by the action of tetrachloride of carbon and alcoholic potash on pyrrol. It melts at  $191^\circ$ , and differs from the  $\beta$ -acid in forming a soluble lead salt. On heating with acetic anhydride the substance pyrocoll



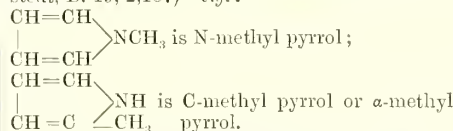
is formed, which is a product obtained by distilling gelatine (B. 17, 103).

**$\beta$ -Pyrrolcarboxylic acid** is formed by fusing  $\beta$ -methyl pyrrol with potash. It crystallises in fine needles, melting at  $162^\circ$ , and forms an insoluble lead salt.

**N-Acetylpyrrol**  $\text{C}_4\text{H}_4\text{NC}_2\text{H}_5\text{O}$ , by the action of acetyl chloride on potassium pyrrol, is an oil boiling at  $178^\circ$ . It is decomposed by alkalis into pyrrol and acetic acid (B. 16, 2,352).

**C-Acetylpyrrol**  $\text{C}_4\text{H}_4\text{C}_2\text{H}_5\text{O}(\text{NH})$  is formed, together with the foregoing, by acting on pyrrol with acetic anhydride. It melts at  $90^\circ$  and boils at  $220^\circ$ , but is not decomposed by alkalis.

*Nomenclature of pyrrol derivatives* (Dennstedt, B. 19, 2,187)—e.g.:

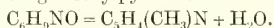


**Pyridine**  $\text{C}_5\text{H}_5\text{N}$  is contained in that fraction of the basic oils of bone oil which boils below  $120^\circ$ , but is also found in smaller quantities in the higher fractions. It can be separated in these by means of its picrate  $\text{C}_5\text{H}_5\text{N.C}_6\text{H}_3(\text{NO}_2)_3\text{OH}$ , which melts at  $162^\circ$ . It is not easily acted on by oxidising agents, and can be separated by this means from the other components of the fraction.

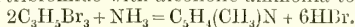
It is formed from all pyridinecarboxylic acids by distilling with lime.

The following are some of the synthetic methods for preparing pyridine and its homologues.

1. Acrolein ammonia, on heating, gives off water yielding methylpyridine



2. The same compound is formed by heating allyl tribromide with alcoholic ammonia to  $250^\circ$

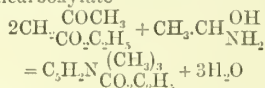




3. Glycerine and acetamide, on heating with phosphorus pentoxide, yield methylpyridine (B. 15, 528).

4. Potassium pyrrol, on heating with chloroform, yields chloropyridine.

5. Ethylic acetoacetate, heated with aldehyde ammonia, gives ethylic trimethyl-dihydropyridin-dicarboxylate



(B. 17, 1,521).

Pyridine is a liquid with a pungent smell, miscible with water; sp.gr. .986 at 0°, and boils at 116.7°. It forms a hydrochloride  $\text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ , and a platinochloride  $(\text{C}_5\text{H}_5\text{NHCl})_2\text{PtCl}_4$ . Sodium amalgam yields piperidine, i.e. hexahydropyridine, which is reconverted into pyridine on oxidation. It forms an ammonium iodide with alkyl iodides, and with chloroacetic acid a pyridine-betaine  $\text{C}_5\text{H}_5\text{N} \left\langle \begin{array}{c} \text{CH}_2 \\ \text{CO} \end{array} \right.$ . By the action

of sodium on pyridine a dipyrindine  $\text{C}_{10}\text{H}_{10}\text{N}_2$  is obtained, an oil boiling at 286–290°, which on oxidation with permanganate yields isonicotinic acid. Together with dipyrindine a body *p*-dipyrindyl is formed  $\text{NC}_5\text{H}_4\text{C}_5\text{H}_4\text{N}$ , which melts at 114° and distils at 304°. It also yields isonicotinic acid on oxidation, and on reduction with tin and hydrochloric acid forms isonicotine, which melts at 78° (B. 16, 423).

The isomeric *m*-dipyrindyl is obtained from *m*-dipyrindyl-dicarboxylic acid (by oxidising phenanthroline). It boils at 293°, and yields on reduction with tin and hydrochloric acid *nicotidine*  $\text{C}_{10}\text{H}_{11}\text{N}_2$ , which boils at 288° (B. 16, 2,521).

On heating pyridine with concentrated sulphuric acid to 300°  $\beta$ -pyridine-sulphonic acid is obtained. The sodium salt of this acid, distilled with potassium cyanide, yields  $\beta$ -pyridyl cyanide, which on hydrolysis forms nicotinic acid.

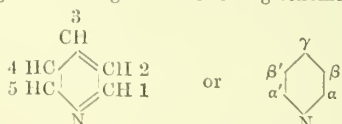
The three possible hydroxy-pyridines are known:—

$\alpha$ -Hydroxypyridine, by distilling the silver salt of hydroxyquinolinic acid; melts at 107°, and is coloured red by ferric chloride.

$\beta$ -Hydroxypyridine is formed from the  $\beta$ -sulphonic acid by fusing with potash. It melts at 123°, and is also coloured red by ferric chloride.

$\gamma$ -Hydroxypyridine or pyridone (which is probably not a hydroxyl- but a carbonyl-compound) is obtained from hydroxypicolinic acid with evolution of  $\text{CO}_2$ . It melts at 148°, and is coloured yellow by ferric chloride (B. 17, Ref. 169).

Pyridine can be represented as a benzene ring in which one CH group is replaced by nitrogen according to the following scheme:



Armstrong proposes to represent the nitrogen by placing a star as shown below:



The positions 1, 5 and 2, 4 are known as ortho- and meta-, and 3 as the para- position. Hence three mono-derivatives of pyridine are possible. The position of the substituting groups in these isomerides has been proved by means of the phenylpyridines obtained from the naphthaquinolines (M. 4, 437; B. 17, 1,518).

#### PYRIDINE MONOCARBOXYLIC ACIDS $\text{C}_5\text{H}_4\text{NCO}_2\text{H}$ .

$\alpha$ -Pyridinecarboxylic acid (1 or ortho-). Picolinic acid was first obtained by oxidising  $\alpha$ -picoline. It is easily soluble in water, crystallises in white needles, melts at 136° and sublimes. By the action of sodium amalgam ammonia is given off with the formation of an acid  $\text{C}_5\text{H}_4\text{O}_3$  (Oxysorbinic acid).

$\beta$ -Pyridinecarboxylic acid (2 or meta-), called nicotinic acid, from the fact of being first obtained by oxidising nicotine, is obtained further from  $\beta$ -methyl- or ethyl-pyridine, from  $\beta$ -pyridyl cyanide, and from three dicarboxylic acids of pyridine (quinolinic acid, cinchomeronic acid, and isocinchomeronic acid), which on heating give off carbon dioxide. It crystallises in needles and melts at 229°.

$\gamma$ -Pyridinecarboxylic acid (3 or para-). Isonicotinic acid is obtained from the dicarboxylic acids, cinchomeronic acids, and lutidinic acid. It melts at (299°) (309°), and crystallises from hot water in fine needles.

#### HYDROXYPYRIDINE-MONOCARBOXYLIC ACIDS.

Several of these acids have been prepared either synthetically, e.g. by heating komanic acid  $\text{C}_8\text{H}_6\text{O}_4$  with ammonia, or from the dicarboxylic acids by splitting off 1 mol. of carbon dioxide (B. 17, 589).

Komenaminic acid  $\text{C}_8\text{H}_7(\text{OH})\text{NCO}_2\text{H}$  is obtained by boiling komanic acid  $\text{C}_8\text{H}_6\text{O}_4$  with ammonia. It decomposes at 270° into carbon dioxide and dihydroxypyridine.

#### PYRIDINE-DICARBOXYLIC ACIDS $\text{C}_5\text{H}_3\text{N}(\text{CO}_2\text{H})_2$ .

Quinolinic acid ( $\alpha\beta$ , or 1.2) is formed by oxidising quinoline. It melts at 225°, and decomposes into carbon dioxide and nicotinic acid.

Cinchomeronic acid ( $\beta\gamma$ , or 2.3) is formed by the oxidation of the quinine alkaloids with nitric acid, or from  $\beta\gamma$ -methyl-pyridinecarboxylic acid on oxidation with permanganate. It melts at 259°, decomposing into carbon dioxide,  $\gamma$ -pyridinecarboxylic acid, and some nicotinic acid.

Lutidinic acid ( $\alpha\gamma$ , or 1.3) is obtained, together with some isocinchomeronic acid, by oxidising lutidine. It melts at 219°, decomposing into carbon dioxide and  $\gamma$ -pyridinecarboxylic acid.

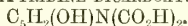
Isocinchomeronic acid ( $\beta\alpha'$ ) melts at 236°, decomposing into carbonic acid and nicotinic acid (Werdel and Herzig, Wiener Akad. B. 1879, 825).

Dicarboxylic acid ( $\beta\beta'$ ). By heating to 150° the lutidinedicarboxylic acid obtained by the condensation of isobutylaldehyde, ethylic acetoacetate and ammonia. The acid does not melt at 285° (Hantzsch and Weiss, B. 19, 284). It is known as dinicotinic acid.

Dicarboxylic acid ( $\alpha\alpha'$ ) or Dipicolinic acid. Obtained by oxidising the lutidine boiling at

146°. This lutidine was found in a fraction of bone oil examined by Ladenburg and Roth (B. 18, 52). It was obtained synthetically by the condensation of cinnamic aldehyde with ethylic acetoacetate and ammonia. The ethylic benzylidene-hydrocollidine-dicarboxylate yields on hydrolysis and oxidation lutidinetricarboxylic acid, and this on distillation with lime gives the lutidine above referred to (Epstein, A. 231, 32).

#### HYDROXYPYRIDINE-DICARBOXYLIC ACIDS



**Hydroxyquinolinic acid**  $[OH:(CO_2H)_2 = (\alpha':\beta)]$ . By fusing quinolinic acid with potash. It blackens without melting at 254° (B. 16, 2,158). Heated with water to 195° it decomposes into carbon dioxide and hydroxypyridine-carboxylic acid. Its silver salt on heating yields  $\alpha$ -hydroxypyridine (B. 17, 592).

**Ammoniochelidonic acid** is obtained by heating chelidonic acid with ammonia.

#### PYRIDINE-TRICARBOXYLIC ACIDS $C_5H_3N(CO_2H)_3$

**$\alpha\beta\gamma$ -Tricarboxylic acid** is formed by completely oxidising the quinine alkaloids, further from  $\gamma$ -methylquinoline and from  $\gamma$ -quinoline-carboxylic acid. It melts at 250°, but begins to decompose at 180° into carbon dioxide and einchomeronic acid.

**$\alpha\beta\beta'$ -Tricarboxylic acid** is obtained from  $\beta$ -quinolinecarboxylic acid. It softens at about 150°.

Tricarboxylic acids have also been obtained by oxidising the alkaloid berberine, and also from uvitonic acid, the condensation product of pyruvic acid and ammonia.

#### PYRIDINE-TETRACARBOXYLIC ACIDS $C_5HN(CO_2H)_4$

**$\alpha\beta\alpha'\beta'$ -Tetracarboxylic acid**. By oxidising the lutidine-dicarboxylic acid formed by the condensation of isobutylaldehyde with ethylic acetoacetate and ammonia (Haantzsch and Weiss, B. 19, 284).

The acid obtained by oxidising collidine-monocarboxylic acid crystallises with 2 molecules of water and melts at 188° (A. 225, 133).

**Pyridine-pentacarboxylic acid**  $C_5N(CO_2H)_5$  from trimethylpyridine-dicarboxylic acid.

A dibromopyridine ( $\beta\beta'$ ) has been obtained by acting on collidine-dicarboxylic acid with bromine and afterwards removing the carboxyl groups (Pfeiffer, B. 20, 1,349). It is identical with that obtained by acting on pyridine with bromine (Hofmann, B. 12, 988).

**Picoline (methylpyridine)**  $C_5H_4(CH_3)N$ . For the separation of this base from the bone oil that portion of the oil is taken which boils between 130°–145°. On subjecting this to redistillation the greater part of the oil comes over between 133–139°. It is not possible to effect a separation of the bases by means of fractional distillation, but a difference in the solubility of the platinum salts of the two bases furnishes a means of separating them. According to Ladenburg (B. 1885, 47) commercial picoline consists of three bases,  $\alpha$ -methylpyridine,  $\beta$ -methylpyridine, and probably  $\alpha\alpha'$ -dimethylpyridine, the second only being present in very small quantities. The same observer (B. 1885, 51) has also noticed the presence

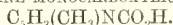
of pyridine in this fraction. It can be separated by means of its picrate, which melts at 162°.

**$\alpha$ -Methylpyridine** boils at 133.9°, is an optically inactive oil, and on oxidation yields picolinic acid.

**$\beta$ -Methylpyridine** boils at 140.1°, and on oxidation yields nicotinic acid. It also differs from the  $\alpha$ -derivative in being slightly levorotatory.

**$\gamma$ -Methylpyridine** does not appear to be contained in bone oil. It has been obtained synthetically by the action of heat on acrolein-ammonia, and also from allyl tribromide.

#### PICOLINE-MONOCARBOXYLIC ACIDS



**Picolinecarboxylic acid** is formed from uvitonic acid, the product of condensation of pyruvic acid and ammonia. It sublimes without melting, and yields on oxidation pyridine-dicarboxylic acid.

#### $\beta\gamma$ -Methylpyridine carboxylic acid

$(CH_3:CO_2H = \gamma:\beta)$  is obtained by heating methylquinolinic acid to 170°. It melts at 210°, and yields on oxidation einchomeronic acid.

#### PICOLINE-DICARBOXYLIC ACIDS $C_5H_2(CH_3)N(CO_2H)_2$

##### Methylquinolinic acid

$((CO_2H)_2:CH_3 = \alpha:\beta:\gamma)$ . By oxidising  $\gamma$ -methylquinoline with permanganate. It melts at 186°, giving carbon dioxide and  $\gamma$ -methyl- $\beta$ -pyridine-carboxylic acid.

**Uvitonic acid** is the condensation product obtained from pyruvic acid and alcoholic ammonia. It melts at 244°, splitting up into carbon dioxide and picolinecarboxylic acid.

**Picoline-dicarboxylic acid** from aldehyde, the condensation product of ethylidene chloride and aldehyde ammonia. It sublimes easily without melting.

A picoline-tetracarboxylic acid is also obtainable from the dicarboxylic acid of collidine by oxidation of the methyl groups with permanganate. Lutidine-tricarboxylic acid is formed as an intermediate product.

**Lutidine (dimethylpyridine)**. The bases having this constitution are for the greater part contained in that portion of the basic oil boiling between 150–170°. After redistilling it is separated into the two fractions 150–160° and 160–170°. The position of the methyl groups in these two fractions is determined by means of the oxidation products formed. The first fraction yields on oxidation iso-einchomeronic acid, which melts at 236°. On heating, carbon dioxide is split off and nicotinic acid is formed. From this is inferred that the position of the two methyl groups is  $\alpha/\beta$ . The higher fraction yields lutidinic acid on oxidation, and this, on heating, gives isonicotinic acid, from which it follows that the methyl groups have the positions  $\alpha\gamma$ . All the acids give pyridine on distillation with lime. According to the researches of Ladenburg and Roth (B. 18, 49), the fraction 139–142° also contains a lutidine, which was separated by means of the mercuric chloride salt, melting at 186°. This was decomposed with potash, and distilled, when, after drying, an oil was obtained which boiled at 142–143°, and yielded on oxidation with per-

manganate a dibasic acid which is identical with that obtained from synthetical lutidine obtained by condensing cinnamic aldehyde, ethylic aceto-acetate, and ammonia (Epstein, A. 231, 1). Its sp.gr. is .9545, and boiling-point 143°.

The constitution of the  $\beta$ -lutidine is



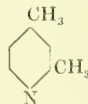
(Ladenburg and Roth).

**Lutidine-monocarboxylic acid** ( $\alpha\alpha'$ -dimethylnicotinic acid). Obtained by distilling lutidine-dicarboxylic acid (Weiss, B. 19, 1,308). It crystallises in fine needles melting at 160°.

**Lutidine-dicarboxylic acid.** Obtained by the condensation of isobutylaldehyde, ethylic acetoacetate, and ammonia (Engelmann, A. 231, 51; Hantzsch and Weiss, B. 19, 284).

**Lutidine-tricarboxylic acid** is formed by the oxidation of collidine-dicarboxylic acid with permanganate.

**$\alpha$ -Lutidine** (so-called). Separated by adding mercuric chloride to a solution in hydrochloric acid of the base boiling at 158-160°. The salt has the composition  $C_8H_9N$ , HCl,  $2HgCl_2$ ,  $\frac{1}{2}H_2O$ , and melts at 130°. On distilling with potash the salt is decomposed, and the base after drying boils at 157°. Its sp.gr. is .9503 at 0° compared with water at 4°. It yields a pyridine-dicarboxylic acid on oxidation with permanganate, and the acid melts at 235°. This is known as  $\alpha$ -lutidinic acid or  $\alpha\gamma$ -pyridine-dicarboxylic acid, since on heating carbon dioxide is given off and isonicotinic acid is formed. Hence  $\alpha$ -lutidine has the composition



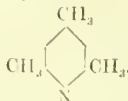
(Ladenburg and Roth, B. 18, 913).

**Collidine** (*trimethylpyridine*)  $C_8H_9(CH_3)_3N$ .

A base of the formula  $C_8H_9N$  has been isolated from the fraction boiling between 170° and 180°, but this has been shown by Weidel and Pick to be an  $\alpha\gamma$ -methylene-pyridine from the fact of its giving on oxidation lutidinic acid melting at 219°. The base is more soluble in cold than in hot water. Its sp.gr. is .9286 at 16.8°; it boils at 178.7° (Weidel and Pick, M. 5, 656). These authors are of opinion that Anderson's collidine (Phil. Mag. 4, 9, 145, 214) was impure. The base does not form any crystallised salts, and is not identical with any synthetical collidine.

**Synthetical collidine.** *Aldehydine.* Formed by the condensation of ethylidene chloride with ammonia (Dürkop, B. 18, 921). It boils at 176°, and its sp.gr. at 0° compared with water at 4° is .9319.

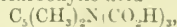
Collidine obtained by distilling with lime the condensation product of ethylic acetoacetate and aldehyde-ammonia. It boils at 171-172°, and has the constitution



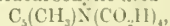
**Collidine dicarboxylic acid.** Is obtained by oxidising hydrocollidine-dicarboxylic acid with

nitrous acid. The ether of this acid is the product of condensation of ethylic acetoacetate with aldehyde-ammonia. It yields on heating with lime  $\alpha\alpha'\gamma$ -trimethylpyridine. The acid yields by successive oxidation of the methyl groups permanganate with the following carboxylic acids:

Lutidine-tricarboxylic acid



Picoline-tetracarboxylic acid



Pyridine-pentacarboxylic acid  $C_5N(CO_2H)_5$ .

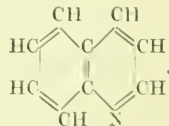
If one carboxyl group be removed from the original acid and it be then oxidised, the following acids are successively obtained:

From collidine-monocarboxylic acid

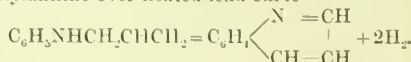
$C_8H(CH_3)_2NCO_2H$  the acids lutidine-dicarboxylic acid  $C_8H(CH_3)_2N(CO_2H)_2$ , picoline-tricarboxylic acid  $C_8H(CH_3)N(CO_2H)_3$ , pyridine-tetracarboxylic acid  $C_5HN(CO_2H)_4$ .

**Quinoline.** This base is contained, together with its homologues, in the higher fraction of the basic oils. The bases are separated by means of the platinum salts from which the platinum is precipitated by means of hydrogen sulphide and the bases liberated by means of potash. The bases accompanying quinoline are lepidine (methylquinoline) and cryptidine (dimethylquinoline).

Quinoline stands in the same relation to naphthalene that pyridine does to benzene. Its constitution may therefore be represented as follows:

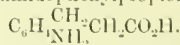


It has been obtained synthetically by passing allylaniline over heated lead oxide

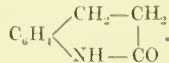


Similarly acrolein-aniline yields on distillation the same base.

Its constitution was determined by its formation from *o*-amidophenylpropionic acid



This gives off water forming hydrocarbostyryl, the constitution of which is



By the action of  $PCl_5$  on this substance dichloroquinoline is formed  $C_6H_5 \begin{matrix} \diagup \text{CH} = \text{CCl} \\ \diagdown \text{N} = \text{CCl} \end{matrix}$  and this on

reduction with hydriodic acid yields quinoline. Very many synthetic methods have latterly been discovered for the formation of quinoline homologues.

1. The condensation of *o*-amido-compounds which contain an oxygen atom joined to the  $\gamma$ -carbon atom in the side chain, e.g. *o*-amido-cinnamic aldehyde.

2. Skraup's synthesis appears to be applicable to all aromatic amines. It consists in heating the amine with glycerine and sulphuric acid in presence of an oxidising agent which is generally nitrobenzene. The equation representing this is



$C_6H_5NH_2 + C_6H_5(OH)_3 = C_6H_5NC_6H_4 + 3H_2O + H_2$ . It is evident that by taking derivatives of aniline or homologues, quinolines substituted in the benzene ring will be obtained.

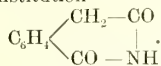
3. Paraldehyde also acts on aromatic amines in presence of sulphuric acid with the formation of methylquinoline, the methyl group being attached to the carbon next to the nitrogen. This methylquinoline is known as quinaldine.

4. Orthoamidobenzaldehyde forms quinolines on condensation with aldehydes or ketones in presence of potash.

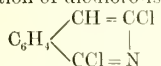
Besides ordinary quinoline an isoquinoline is known in which the nitrogen atom takes the place of the CH group in naphthalene in the  $\beta$ -position instead of in the  $\alpha$ -position as in ordinary quinoline. The iso-derivative occurs in the quinoline derived from coal tar and it is owing to the presence of this compound that the dyestuff quinoline-red is formed (Hofmann, B. 20, 4).

Isoquinoline has been obtained as follows:

The ammonium salt of *o*-carboxyphenylacetic acid is heated until no more ammonia or water is given off. The homo-*o*-phthalimide remaining behind is then distilled in a vacuum and has the constitution



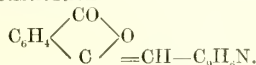
This is then heated with phosphorus oxychloride with the formation of dichloro-isoquinoline



and this on reduction with concentrated hydriodic acid yields isoquinoline (Gabriel, B. 19, 2,354).

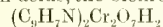
A mixture of quinoline and lepidine ( $\gamma$ -methylquinoline) treated with anil iodide yields the dyestuff known as cyanine.

Quinaldine on heating with phthalic anhydride yields quinophthalone, which probably has the constitution



On treating this with fuming sulphuric acid a sulphinate is formed which is a dyestuff known as quinoline yellow.

Quinoline is a colourless strongly refractive liquid boiling at  $236^\circ$ , sp.gr. at  $20^\circ$  1.0917. It forms salts with acids, the bichromate



melting at  $165^\circ$  being especially characteristic.

Nascent hydrogen converts it into dihydroquinoline  $C_9H_9N$ , melting at  $161^\circ$ , and tetrahydroquinoline boiling at  $245^\circ$ . On heating quinoline with sodium, so-called  $\alpha$ -diquinoline melting at  $170^\circ$  is formed. The  $\beta$ -product melting at  $192^\circ$  is formed by heating quinoline with benzoyl chloride or by distilling  $\gamma$ -quinoline-carboxylic acid with lime.

Substitution products of quinoline with the substituting groups in the benzene ring are formed from the substituted anilines by Skraup's synthesis; such for example are the chloro-, bromo-, and nitro-quinolines, and also the quinoline-sulphonic acids. These latter yield cyanides on distillation with potassium cyanide, which in turn form carboxylic acids on hydrolysis.

**Hydroxyquinolines**  $C_9H_7(OH)N$ . Those containing the OH group in the benzene ring are ob-

tained synthetically from the amido-phenols or by fusing the quinoline-sulphonic acids with potash.

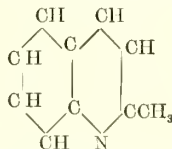
*o*-Hydroxyquinoline melts at  $75^\circ$  and boils at  $258^\circ$ . On reduction with tin and hydrochloric acid hydroxytetrahydroquinoline is formed, and this by treating with methyl iodide forms hydroxytetrahydromethylquinoline, the hydrochloride of which is kairine, its formula being  $C_{10}H_{13}ON, HCl, H_2O$ .

*m*-Hydroxyquinoline is obtained from *m*-amido-phenol or from the corresponding quinoline-sulphonic acid. It melts at  $238^\circ$ .

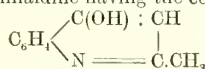
*p*-Hydroxyquinoline from *p*-amidophenol or from the quinoline-sulphonic acid obtained from sulphanic acid. The most important of the hydroxyquinolines containing the hydroxyl group in the pyridine ring is carbostyrl. This is obtained by reducing ethylic *o*-nitrocinnamate with ammonium sulphide. It crystallises in prisms or fine needles and melts at  $199^\circ$ . On oxidation with permanganate it forms oxalyl-anthranilic acid.

**Homologues of quinoline.** The three toluidines all yield methylquinolines which on oxidation give quinolinic acid, the benzene ring being destroyed.

Quinaldine ( $\alpha$ -methylquinoline) has the constitution:

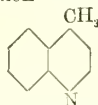


and was first obtained by the condensation of aniline with acetaldehyde by means of sulphuric acid. It is also formed by acting on *o*-amido-benzaldehyde with acetone and caustic potash. Coal tar quinoline contains about 25 p.c. of this base. It boils at  $239^\circ$  and yields according to the oxidising agent used either  $\alpha$ -quinolinecarboxylic acid or acetylanthranilic acid. Anilacetoacetic acid on condensation yields  $\gamma$ -hydroxyquinaldine having the constitution



a substance boiling at  $222^\circ$ .

Lepidine  $\gamma$ -methylquinoline, which appears to be identical with so-called iridoline from coal tar, is formed by distilling cinchonine with lime. It has the constitution



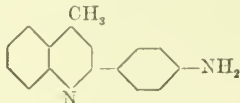
which is proved by oxidising it with permanganate, the first product being methylquinolinic acid, and the final one ( $\alpha$ - $\beta$ - $\gamma$ -) pyridine-tricarboxylic acid.

Dimethylquinolines are formed by condensing the three toluidines with paraldehyde or from the xylidines by heating with glycerine.

Phenylquinoline ( $C_6H_5$  in the benzene ring) is formed from *p*-amidodiphenyl on condensation with glycerine.

*o*-Phenylquinoline ( $C_6H_5$  in the *o*-position to the nitrogen) is formed by heating cinnamaldehyde and aniline with hydrochloric acid.

*m*-Phenylquinoline by condensing *o*-amido-benzaldehyde with phenylacetaldehyde. Flavvaniline, a yellow dyestuff formerly employed, is also a quinoline derivative. It is formed by heating acetanilide with zinc chloride to 260°. Its constitution is



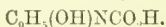
but owing to not being fast to light, it is no longer in use.

#### Quinoline-carboxylic acids $C_9H_7NCO_2H$ .

Those containing the carboxyl group in the benzene ring can all be formed from the amido-benzoic acids or by saponification of the cyan-quinolines obtained from the quinoline-sulphonic acids.

Those acids containing the carboxyl group in the same ring as the nitrogen are formed by oxidising methyl- or ethyl-derivatives of quinoline in which the substituting group is in that ring. Thus quinaldine yields  $\alpha$ -quinolinecarboxylic acid or quinaldic acid on oxidation with chromic acid, and the  $\beta$ -carboxylic acid is formed from  $\beta$ -ethylquinoline which on oxidation with permanganate gives  $\alpha\beta\beta'$ -pyridine-tricarboxylic acid. Cinchonic acid or  $\gamma$ -quinolinecarboxylic acid is formed by oxidising cinchonine with permanganate or  $\gamma$ -methylquinoline with chromic acid.

#### Hydroxyquinolinecarboxylic acids



These are formed by fusing the sulphonic acid of the corresponding quinoline-carboxylic acid with potash.  $\alpha$ -Hydroxy- $\beta$ -quinolinecarboxylic acid is obtained by condensing *o*-amido-benzaldehyde with malonic acid.

*Literature*.—Anderson, T. R. S. E. 16, 463; 20, 247; 21, 219; 21, 571; A. 70, 32; 84, 44; 94, 358; 105, 335. Weidel, S. W. A. 79, 837; 80, 443; 80, 821; 81, 512; 90, 972; B. C. G. 12, 1, 989; 13, 65. Ladenburg, B. 18, 47. Ciamician, B. 14, 1, 051.

**BOOKUM or SAPPAN WOOD.** An Indian wood, the product of *Cesalpinia sappan*. Used in dyeing reds.

**BOOMAH NUTS.** The fruit of *Pyrenocoma macrophylla*, belonging to the Euphorbiaceæ. Used in tanning (Holmes, Ph. [3] 8, 363).

#### BORACIC or BORIC ACID *v.* BORON.

**BORACITE** *v.* BORON.

**BORAX** *v.* BORON.

#### BORDEAUX *v.* AZO-COLOURING MATTERS.

Lambert (Fr. 22, 46) detects this dye in wines by precipitating with basic lead acetate, and extracting the precipitate with alcohol; the red solution thus obtained is turned yellow by alkalis. Wool heated with the wine withdraws its colouring matter.

Bellier (J. Ph. [5] 14, 7) describes a method of determining quantitatively the amount of this dye in wines.

#### BORNEO CAMPHOR *v.* CAMPHOR.

**BORNEOL** *v.* CAMPHORS.

**BORNESIT** *v.* GLUCOSIDES.

**BORNITE or PURPLE COPPER ORE.** A double sulphide of copper and iron of variable composition, found in Cornwall, Ireland, Chili, and Canada. Known also as *Erubescite*, in allu-

sion to its power of becoming tarnished. Called by the Cornish miners 'horse-flesh ore.'

**BORACALCITE.** Calcium dimetaborate. It is found on the plains of Iquique, Ecuador, South America.

**BORO-GLYCERINE.** An antiseptic, patented by Barff (Ger. Pat. 18,108; Eng. Pat. 5,096, 1884); prepared by heating 92 parts glycerol with 62 parts boric acid at 200°C. It is a yellowish, transparent substance, soluble in alcohol and in 40 parts of water. Used as a preservative for fruits and wines (S. C. I. 1, 244; 4, 362).

**BORON.** B. At. w. 10.97. An element usually reckoned among the metalloids, although it presents analogies to the metals, and has been placed by Etard (C. R. 91, 627) at the head of the vanadium group, intermediate between that of phosphorus and that of carbon; is a triad in most of its known combinations, but is also capable of acting as a pentad (Michaelis and Becker, B. 13, 58). Never occurs free; usually as boric acid, and in several minerals, as *borax* or *tincal*, *boracite*, *hydroboracite*, *rhodizite*, *sas-solin*, *boracalcite*, *boronatrocalcite*, *datolite*, and *botryolite*, and in small quantities in *schorl*, *ap-yrite*, and *axinite*.

The element was first isolated by Gay-Lussac and Theuard in 1808, by heating boric oxide with potassium, boiling out the fused mass with hydrochloric acid and washing with water. According to Wöhler and Deville (A. Ch. [3] 52, 63) it may be obtained by mixing 60 grams of sodium in small pieces with 100 grams of powdered boric oxide in an iron crucible, covering the mixture with a layer of 30 grams ignited sodium chloride in fine powder, and heating the whole to redness. After the completion of the reaction, which is very violent, the mixture is stirred with an iron rod, until the sodium and sodium chloride are fused, and carefully poured into dilute hydrochloric acid, and the residue washed with water containing ammonium chloride (which salt is subsequently removed by alcohol) and dried. Boron can also be obtained by heating potassium borofluoride with potassium (Berzelius), or magnesium (Wöhler and Deville); by the electrolysis of fused boric oxide (Davy); by reducing boron trichloride by hydrogen (Dumas); by fusing borax with amorphous phosphorus (Dragendortf); by heating boric oxide with magnesium and treating the residue with dilute hydrochloric acid.

All these processes yield boron as an opaque amorphous powder of a greenish-brown colour; it is tasteless, odourless, staining the fingers strongly; becomes denser on being heated in a vacuum or in gases which have no action upon it; non-conductor of electricity; not oxidised at ordinary temperatures in either air or oxygen; heated in air it burns with a reddish light, forming  $B_2O_3$  and BN; burns with dazzling brightness in oxygen, forming  $B_2O_3$ . Boiling water has no action on it, but it is readily oxidised by strong nitric acid in the cold, and by sulphuric acid when heated. When heated to redness with the alkaline salts of oxyacids, yields an alkaline borate, the formation being frequently attended with incandescence, and in the case of nitre with explosion. Heated with potash it forms potassium borate with liberation of hydrogen, and reduces the chlorides of gold, mercury, silver, and lead and

sulphide of lead, chloride and sulphide of boron being formed (Wöhler and Deville, *L.c.* and A. 105, 72). Heated in nitrogen it forms white boron nitride. It decomposes nitric oxide at a red heat, burning brilliantly and forming boric oxide and nitride, but apparently has no action on nitrous oxide.

The only industrially important compounds of boron are boric oxide, boric acid, and certain borates.

**Boric Oxide**  $B_2O_3$ . Obtained by burning boron in oxygen, or, more easily, by strongly heating boric acid, when it melts at  $577^\circ$  to a viscid mass, cooling to a colourless brittle glass of sp.gr. 1.83. Non-volatile and hence capable of expelling carbonic, nitric, and sulphuric acids from their salts at a red heat. Soluble in water, forming boric acid.

**Boric or Boracic Acid.** *Sal sedativum Hombergii*, *Sal narcoticum vitrioli*. Boric oxide forms three hydrates:

Orthoboric acid  $B_2O_3 \cdot 3H_2O = H_3BO_3$ .

Metaboric acid  $B_2O_3 \cdot H_2O = H_2BO_3$ .

Pyroboric acid  $2B_2O_3 \cdot H_2O = H_2B_4O_7$ .

Boric acid appears to be a bibasic acid, and most of its salts may be regarded as derived from metaboric or pyroboric acid. Both these are so-called 'weak' acids. Their salts, when soluble, have usually an alkaline reaction, even when containing excess of boric acid, and are decomposed even by carbonic acid.

Boric acid is found free in nature in many volcanic districts—as in Tuscany, where the vapours issuing from the earth are charged with the acid, which is found dissolved in the small lakes (*laguni*) formed by the condensation of the vapours, or deposited as a crystalline crust round their margins—as in the neighbourhood of Sasso. In smaller quantities it exists in sea-water and in many mineral springs. The most important natural borates are *borax* or *tincal*, *boracite*, *datolite*, and *boronatrocalcite*.

Pure boric acid is easily obtained by treating a solution of 3 parts borax in 12 parts hot water with 1 part sulphuric acid. On cooling, boric acid separates out; it is recrystallised from hot water, dried and fused to expel traces of sulphuric acid, and again recrystallised from water. It forms white, translucent, monoclinic laminae (Kengott), which have a mother-of-pearl lustre and are unctuous to the touch. Sp.gr. 1.434 at  $15^\circ$ . 1 part dissolves in 25.7 parts water at  $18^\circ$ , 14.9 parts at  $25^\circ$ , 10.7 parts at  $50^\circ$ , 4.7 parts at  $75^\circ$ , and 2.97 parts at  $100^\circ$  (Brandes and Firnhaber, *Ar. Ph.* 7, 50). More soluble in alcohol and volatile oils. Its solubility in water is increased by the presence of tartrates or tartaric acid. A cold saturated solution of boric acid colours litmus a wine-red; a hot saturated solution gives a bright-red colour. Turmeric paper moistened with an alcoholic solution of boric acid acquires a brown-red tint, which is intensified by acids and turned greenish-black by alkalis. The alcoholic solution burns with a green flame, especially when acidified by sulphuric or hydrochloric acid.

Crystallised boric acid, heated to  $100^\circ$ , is converted into  $H_2B_4O_7$  (Schaffgotsch, *J.* 1859, 71), and into  $H_2B_6O_{11}$  at  $160^\circ$  (Merz, *J. pr.* 99, 179; Ebelmen and Bouquet, *A. Ch.* [3] 17, 63). At a stronger heat the acid froths up, parting with its

water and forming boric anhydride as a fused viscid mass, solidifying to a fissured glass on cooling.

The chief use of boric acid is in the manufacture of borax (*q. v.*). It is also employed for glazing porcelain, in the preparation of glass and certain pigments, and for soaking the wicks of stearine candles. It has also been proposed to use boric acid in the preparation of nitric acid from Chili saltpetre, so as to obtain borax as a by-product.

Boric acid has no effect upon vinous fermentation; it retards acetous fermentation, however, but only in those cases where no acetic acid is already present (Herzen, *B. C.* 1880, 487).

**Industrial extraction of boric acid.** The occurrence of the *sal sedativum* of Homberg in the water of the Tuscan lagoons appears to have been first noticed in 1777 by Höfer, a Florentine apothecary, and its extraction was begun about 1815, and to-day the greater part of the boric acid of commerce is derived from the lagoons near Monte Rotondo, Lago Zolforeo, Sasso, and Larderello, in the Maremma of Tuscany, inclosing both natural and artificial vents. The *soffioni* or jets of steam, which often rise in thick columns to a considerable height, contain only traces of boric acid, but when these are condensed in the water of the lagoons this becomes gradually charged with the acid which is obtained from the solution by evaporation.

To obtain the boric acid, the *soffioni* are surrounded by basins of rough masonry, several of which are arranged in steps, one above the other, in such manner that the contents of each basin can be led by gravitation into the basin below. Fresh water from a neighbouring spring is conducted into the uppermost basin, while the gases and vapours of the fumaroles rise through the water from beneath, occasionally with such violence as to eject the water to a height of several feet. After twenty-four hours the water in the first basin, which is generally muddy, is allowed to pass into the second basin, the first being recharged with fresh water. After another twenty-four hours the second basin is discharged into the third and the first into the second, the second and following basins being also built round *soffioni*. After having passed through four or five of these basins, the solution is passed into rectangular reservoirs in which the suspended matter is deposited on standing. From these it passes into a series of leaden evaporating pans, placed in couples one above the other in the form of a terrace. These pans are heated by the gases and vapours of *soffioni*—which on account of their situation are otherwise useless—by a method first adopted by Count Lardarel in 1815. The evaporating pans are square, about 1 foot deep and 9 feet square, and are supported on wooden beams. The solution is heated in these for twenty-four hours until it has attained a density of 1.017, when it is decanted into a second series of pans, where, after another twenty-four hours, it attains a density of 1.034, and is finally decanted into the last four pans, where it is evaporated to a specific gravity of 1.07.

The temperature gradually increases, being in the first pans about  $60^\circ$  to  $71^\circ$ , in the follow-



ing pans about 75°, and in the last as high as 80°.

In all these pans a precipitation of gypsum takes place, which requires to be removed from time to time. When the solution in the last pans has attained a density of 1.07, it is run through funnels into the crystallising vats, consisting of wooden tubs lined with lead. After twenty-four hours the crystallisation is complete, the mother liquor is then decanted off and added to the evaporating pans a few hours before the completion of the concentration. The crystals are drained in baskets placed under the crystallising vats for twenty-four hours, and are spread out on the bottom of a large drying oven, which is likewise heated by the vapour from the soffioni. The layer of crystals, which is two or three inches thick, is stirred at intervals to assist the drying. This is complete in twenty-four hours. An improved form of evaporating apparatus consists in decanting the solution in the reservoirs from which the suspended matter has deposited into a pan, and thence running it into a slightly inclined trough made of sheet lead with the edges turned upwards. The trough has an undulatory form, is supported on wooden sleepers, and heated by the soffioni vapours. The solution of boric acid after passing through this heated trough becomes so concentrated as to be ready for crystallisation.

Artificial soffioni have been bored to a depth of 200 feet in the vicinity of the Monte Rotondo, and yield an annual supply of over 200 tons of boric acid. The chief works are at Monte Cerboli, Larderello, San Federigo, Castel Nuovo, Sasso, Monte Rotondo, Lustignano, Seranzano, Lago, and San Eduardo, each of which has from 8 to 35 *lagni*, 100 to 200 feet in diameter (Payen, Ind. Ch., trans. by Paul).

The boric acid thus obtained is far from pure. Analyses of different samples by Payen, Vohl, and Wittstein show that it contains from 74.80 p.c. crystallised boric acid, from 4.5 to 7 p.c. of hygroscopic water, ammonium and magnesium sulphates 8.14 p.c., together with gypsum, clay, sand, sulphur, organic matter, and free acids and ammonia.

The following table shows the general composition of crude boric acid:

	Wittstein	Payen
Boric acid . . . . .	76.5	74 to 84
Ferric sulphate . . . . .	0.4	—
Aluminium sulphate . . . . .	0.3	—
Calcium sulphate . . . . .	1.0	2.4 to 1.2
(Including clay, sand, &c.).		
Magnesium sulphate . . . . .	2.6	14.0 to 8.0
Ammonium sulphate . . . . .	8.5	
Sodium and potassium sulphates . . . . .	1.3	—
Manganese sulphate . . . . .	trace	—
Ammonium chloride . . . . .	0.2	2.6 to 1.0
Silica . . . . .	1.2	—
Sulphuric acid . . . . .	1.3	—
Hygroscopic water . . . . .	6.6	7 to 5.8

and organic matter.

The origin of the boric acid in the soffioni is not understood. Dumas suggested that it is formed by the decomposition by means of water of a bed of boron sulphide formed at some depth below the surface. Bolley (A. 68, 122)

has supposed that it is produced by the action of a hot solution of ammonium chloride upon the borates contained in the earth. According to Warington (C. G. 1854, 419), Wöhler and Deville (A. 105, 69), and more lately Popp (A. Suppl. 8, 1), its formation is probably due to the action of water upon boron nitride.

Diculafait has found boric acid in regions where there are no visible manifestations of volcanic action, and concludes that it is of aqueous origin, and derived from the waters of ancient seas (C. R. 100, 1,017, and 1,240).

Boric acid occurs on the West Coast of South America, principally in the form of boronatrocalcite (*ulexite*, or *hayesine*), and is found throughout the province of Atacama and in the newly acquired portions of Chili. Ascotan and Maricunga, to the north of Copiapo, are the places which have proved most successful commercially. The crude material, known as *tiza*, occurs in both places in lagoons or troughs; these, instead of being entirely filled with common salt, as is usually the case in the desert, contain zones or layers of boronatrocalcite, alternating with layers of salt and salty earth. The lagoons of Maricunga are estimated to cover 3,000,000 sq. metres. The raw material contains on the average about 25 p.c. of boric acid, but by washing and calcination it may be raised to 55 or 60 p.c. The roughly purified boronatrocalcite is shipped to England and Germany. It is treated with hydrochloric acid and the separated boric acid converted into borax either by the wet way or by fusion with soda ash (Darapsky, C. Z. 11, 605; Lunge, D. P. J. 181, 370).

Volcanic emanations containing boric acid occur in Nevada, in California, and Nova Scotia. A borate of lime (*rhodizite*) is imported from the West Coast of Africa.

#### METALLIC BORATES.

Borates are obtained by the action of boric acid on metallic oxides or their salts, either in the dry or wet way.

In solution boric acid is a very weak acid, being expelled by almost all acids from its combinations, partially so even by carbonic and hydrosulphuric acids. A boiling concentrated solution, however, decomposes carbonates and soluble sulphides and manganese sulphide.

In the dry way, at high temperatures, it is capable of decomposing the salts of all more volatile acids.

Alkaline borates are readily soluble in water, but are precipitated by alcohol. None are perfectly insoluble in water; but all the others, except the borates of the alkaline metals, may be prepared by precipitation.

The sparingly soluble borates are easily decomposed by water. Even the alkaline borates are decomposed by water. A concentrated solution of borax turns blue litmus red; on the addition of a considerable quantity of water the litmus is coloured blue. Dilute solutions of borates behave indeed like dilute solutions of the alkali mixed with boric acid. They absorb carbonic acid from the air, set ammonia free from its compounds, &c. (Rose).

Soluble borates give white precipitates with salts of barium, strontium, calcium, aluminium,

zinc, lead; red with cobalt, green with nickel, yellow (red on boiling) with ferric salts. These precipitates are readily soluble in ammonium chloride; and if they have been produced by an acid borate of an alkali metal, they are soluble in excess of the salt from which they have been precipitated.

For the literature of the borates in general v. WATTS'S DICTIONARY, vol. i. 529. Only the more important salts, or those which have industrial relations, will be here described.

**Ammonium borates.** Only acid salts are known. Of these  $\text{NH}_4\text{BO}_2 \cdot 2\text{HBO}_2 + 1\frac{1}{2}\text{H}_2\text{O}$  occurs as *Larderellite* in the Tuscan lagoons, and may be obtained by dissolving boric acid in warm ammonia. A solution of ammonium borate has been employed for rendering light fabrics non-inflammable.

**Calcium borates.** The *orthosalt*  $\text{CaH}_2\text{BO}_3$  is formed by the addition of limewater to borax. The *sesquimetalborate*  $\text{Ca}_2\text{H}_2\text{B}_2\text{O}_6$  is precipitated together with the dimetalborate  $\text{CaH}_2\text{B}_2\text{O}_5$  by the addition of calcium salts to borax. *Rhodizite* appears to have the composition of the sesquimetalborate, whilst *hayesite*, *borocalcite*, and *hydroborocalcite* are dimetalborates.

**Copper borate.** Bolley (J. 1847-8, 1,059) recommended the use of the green precipitate obtained by the mixture of cold solutions of 2 parts cupric sulphate and 3 parts borax as a substitute for arsenical green in painting and dyeing. V. also Poussier (B. 6, 1,138).

**Iron borate.** Ferric monometaborate  $\text{Fe}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{Aq}$  is found as *cagunite* in the lagoons of Tuscany. Basic salts are formed by precipitating ferric salts with alkaline borates, and by the precipitation of ammonioferric sulphate with sodium monometaborate or borax (Rose).

**Lead borates.** Faraday (P. A. 18, 501) by fusing 1 mol. of lead oxide with 2 mols. of boric oxide obtained a nearly colourless glass, as hard as flint glass, and with a much higher refractive power.

**Magnesium borate.** Magnesium monoborate  $\text{MgBO}_2$  exists native as *boracite*: usually contains also calcium borate. Has been prepared artificially by Heintz (P. A. 110, 613).

**Sodium borate.** *Trisodium orthoborate*  $\text{Na}_3\text{BO}_3$  is formed when boric oxide is fused with excess of caustic soda (Bloxam, Q. C. J. 14, 143). *Tetrasodium borate*  $\text{Na}_4\text{B}_2\text{O}_7$  is formed by fusing borax with excess of sodium carbonate (Arvedson, Gm. 3, 87; Bloxam, Q. C. J. 12, 186). *Sodium monometaborate*  $\text{NaBO}_2$  is produced by heating 62 parts boric acid, or 191 parts borax, with 53 parts of anhydrous sodium carbonate. On dissolving the fused mass in water the trisodium orthosalt  $\text{Na}_3\text{BO}_3 \cdot 3\text{H}_2\text{O}$  separates out in large monoclinic prisms.

*Sodium dimetalborate*, *acid metaborate*, *bi-borate of soda*, or *borax*  $\text{Na}_2\text{B}_4\text{O}_7$ , the most important salt of boric acid, is found native in Transylvania, Peru, California, India, Thibet, Tartary, and Ceylon. The borax of commerce was formerly exclusively obtained from the salt lakes in these countries. The yellowish-white mass of crystals obtained by the evaporation of the water was sent to Europe under the name of *tincal*. It consisted of borax mixed with lime, magnesia, alumina, and chlorides, and sulphates

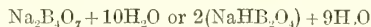
of sodium and calcium, as well as with some greasy substance with which it was coated, ostensibly to protect it from breakage during transport. The purification of the crude substance was conducted more especially in Venice, Hamburg, and certain Dutch seaports. By one method limewater was added to remove the greater part of the greasy substance from the crystals, which were further cleansed by the addition of a 2 p.c. solution of calcium chloride to their solution in hot water. The lime-soap so formed was strained off, and the clear liquid concentrated. Or the powdered tincal was washed in a sieve with a solution of caustic soda of sp.gr. 1.034, dissolved in water and treated with a 12 p.c. solution of soda to precipitate the earths, and, after standing, the solution was evaporated and allowed to crystallise in short conical vessels of wood lined with lead.

According to Clouet (D. P. J. 142, 395) tincal may be refined by calcining it with one-tenth part of sodium nitrate, dissolving in water and crystallising out.

An important source of natural borax is found near the Clear Lake in California, in a body of water now called the Borax Lake. This is situated in a region of hot springs and volcanic action, about 65 miles north-west of Suisan Bay and about 36 miles from the Pacific coast, and was first described by Veatch in 1856. The water contains 2,401.56 grains of solid matter per gallon, of which 535 consist of crystallised borax (G. E. Moore). The bed of the lake consists of borax crystals, which are obtained by sinking caissons, pumping out the water and digging up the deposit.

The greater part of the borax of commerce is prepared from the boric acid of Tuscany. From 110 to 120 parts of crystallised sodium carbonate are dissolved in a lead-lined covered vessel heated with steam, and 100 parts of boric acid are added in small charges, any ammonium carbonate which is evolved being led into sulphuric acid. The solution of borax thus obtained deposits either prismatic or octahedral crystals according to its strength and temperature.

#### 1. Prismatic or ordinary borax



is formed when the solution obtained as above described has a specific gravity (after all the carbonic acid has escaped) of 1.14 to 1.15, and boils at 104°C. It is left to crystallise for two or three days, the crystallisation being completed when the temperature has reached 25°-30°C. The crystals are freed from the mother liquor, treated with sodium carbonate to remove any earths, and the solution evaporated to the same consistency and crystallised in the same manner as before.

An impure borax which is used in glass-making is obtained from the mother liquor.

The crystals should be sponged to remove completely all the mother liquor and dried out of contact with cold air, which causes cracks to form in the crystals. Crystals containing such cracks when heated split in their plane of cleavage, and are inconvenient for use in soldering as they are liable to fly to pieces. This inconvenience may be partially remedied by recryst-

tallisation from a concentrated solution, or better by the addition of a small quantity of tincal before recrystallisation.

Prismatic borax forms large transparent monoclinic prisms with truncated lateral edges. They effloresce when exposed to the air (according to Sims, only when they contain sodium carbonate), they give out light when rubbed in the dark, possess a sweet somewhat cooling alkaline taste, and a specific gravity of 1.75 (1.69 according to Filhol, A. Ch. [3] 21, 415). For their optical properties v. Senarmont (A. Ch. [3] 41, 336) and Tschermak (Sitz. W. 57 [2] 641). When heated they melt in their water of crystallisation, swelling up and solidifying to a spongy mass called burnt or calcined borax (*borax usta*), and fuse at a red heat to a colourless anhydrous glass (vitrified borax) with a specific gravity 2.36, which gradually absorbs water from the air and becomes prismatic borax.

2. A borax with 6 mols. water  $\text{Na}_2\text{B}_4\text{O}_7 + 6\text{H}_2\text{O}$  was found by Beehi (J. 1854, 867) in an old lagoon crater. It has not yet been obtained artificially.

3. Octahedral borax  $\text{Na}_2\text{B}_4\text{O}_7 + 5\text{H}_2\text{O}$  or  $2(\text{NaHB}_2\text{O}_4) + 4\text{H}_2\text{O}$ . The solution obtained as above by Payen and Cartier's method is concentrated to a specific gravity of 1.246, and allowed to cool slowly in a warm place. The crystallisation commences at  $79^\circ\text{C}$ ., and is stopped at  $56^\circ\text{C}$ ., when prismatic borax begins to crystallise out. The mother liquor is quickly siphoned off, and the crystals are removed and dried in the air.

The crystals are regular, transparent octahedra, harder than the ordinary borax. They have a conchoidal fracture and a sp.gr. = 1.8. They do not change in dry air, but absorb moisture very readily and become prismatic. They fuse more readily than the prismatic crystals, and with less intumescence, and without splitting. Octahedral borax is therefore better adapted for soldering and as a flux than common borax, and the smaller quantity of water (a difference of 17 p.c.) diminishes the cost of transport. The prismatic variety is, however, generally preferred, probably because it is cheaper weight for weight.

Gernez (C. R. 78, 68) has investigated the causes determining the formation of the prismatic and octahedral varieties, and states that the latter may be prepared from supersaturated solutions completely protected from dust, and by the evaporation of borax solutions in a vacuum at a temperature of  $10^\circ\text{--}12^\circ\text{C}$ .

Amorphous borax  $\text{Na}_2\text{B}_4\text{O}_7 + 4\text{H}_2\text{O}$  or  $\text{NaHB}_2\text{O}_4 + \text{Aq}$  was obtained by evaporating a solution of borax and drying for some time at  $100^\circ\text{C}$ . (Schweizer, J. 1850, 257).

Artificial borax usually contains some impurities, e.g. sodium carbonate, small quantities of sulphates and chlorides, and of calcium and magnesium salts. It is sometimes adulterated with alum and common salt.

It should dissolve in two parts of hot water and should not effervesce with acids. The aqueous solution should not be rendered turbid when treated with an alkali, or with barium chloride or silver nitrate in the presence of nitric acid.

Borax dissolves readily in water, but is insoluble in alcohol. According to Poggiale, 100 parts of water dissolve—

2.8 parts at	$0^\circ\text{C}$ .
7.9 " "	$20^\circ\text{C}$ .
17.9 " "	$40^\circ\text{C}$ .
40.4 " "	$60^\circ\text{C}$ .
76.2 " "	$80^\circ\text{C}$ .
119.7 " "	$90^\circ\text{C}$ .
201.4 " "	$100^\circ\text{C}$ .

The aqueous solution has a slightly alkaline reaction, and changes the colour of an alcoholic solution of turmeric to brown; a small quantity of sulphuric acid restores the original yellow colour, but a larger quantity sets boric acid free, which reproduces the characteristic brown colouration.

Borax is easily decomposed by acids. A large quantity of water decomposes it slightly, so that a very dilute solution of borax acts like a mixture of the neutral borate and boric acid. *Hydrochloric acid* leaves, on evaporation, sodium chloride and free boric acid. *Carbonic acid* is absorbed by a solution of borax from the air, and no borax is precipitated on the addition of alcohol. Saturated with *sulphuretted hydrogen* and mixed with alcohol, the liquid separates on the addition of ether into two layers, the lower containing sodium sulphide, the upper free boric acid.

It forms double salts with arsenious acid of the empirical formula,  $3\text{Na}_2\text{O} \cdot 6\text{B}_2\text{O}_3 \cdot 5\text{As}_2\text{O}_3 + 10\text{Aq}$ . Schweizer (J. 1850, 257). With *sodium fluoride* it forms sodium fluoborate. When 1 pt. tartaric acid is mixed with 2 pts. of a hot solution of borax, boric acid separates out on cooling. If the tartaric acid be increased, the separation of boric acid likewise increases up to a certain point, after which it diminishes, and ultimately is no longer separated. *Acid tartrate of potassium* forms a double salt with borax. *Silicic acid* is insoluble, or nearly so, in solutions of borax.

*Benzoic, tartaric, and gallic acids* dissolve more readily in borax than in water. Many fatty acids and resins dissolve as readily in borax as in alkaline leys, the borax behaving like a mixture of boric acid and free soda.

At a red heat, however, the boric acid in borax readily dissolves and unites with metallic oxides, forming a fusible glass of a double salt, which property renders it of great use in soldering and in metallurgical operations and in blow-pipe analysis, the glasses thus formed often exhibiting characteristic colours. It is used also in the preparation of easily fusible glass fluxes for enamels and glazes.

An enamelled coating for cast-iron is made by fusing on the metal a mixture of quartz, felspar, clay, and borax, and then covering it with a glaze containing borax.

A mixture of 1 part clay, 1 part felspar, and 2 parts borax is used instead of lead-glaze for glazing for stoneware.

Ebelmen (J. C. 1851, 12) prepared *corundum* by fusing alumina and borax in a porcelain furnace. By fusing borax with titanate acid G. Rose obtained rutile, and with silicic acid he formed *tridymite*. G. Rose (B. A. B. 1867, 130, 450; J. pr. 101, 228, and 108, 208).

When mixed with shellac in the proportion of 1 to 5, borax renders the shellac soluble in



water, and forms with it a kind of varnish. It is also used in medicine both externally and internally, and tartarised borax enters into the composition of some pharmaceutical preparations.

**Borocitrates** are valuable as remedies in cases of kidney disease and urinary calculi. Their solvent power for urates and phosphates is greater than that of lithium benzoate. The diborocitrates being best adapted for the purpose. The following are known:

Magnesium triborocitrate  $(C_6H_5O_7)_2Mg_3(B_3H_3O_6)_2$   
 „ diborocitrate  $(C_6H_5O_7)_2Mg_2(B_2H_2O_5)_2$   
 „ monoborocitrate  $(C_6H_5O_7)_2Mg(BHO_2)$

Lithium, potassium, sodium, and ammonium mono-, di-, and triborocitrates of similar constitution have been prepared. Iron salts have also been obtained containing respectively 8 and 16 p.c. of iron by acting on sodium di- and monoborocitrate with ferric hydrate (Scheibe, Ph. [3] 11, 389).

The magnesium compounds possess strong antiseptic properties according to Schwarz (Sitzungsber. der Dorpater Naturforscher Gesellschaft. 1879, 204).

**Borax as a preservative.** Endemann (C. N. 41, 152) finds that boric acid acts as a preservative to fresh meat only; that previously salted could not be preserved by means of it. He attributes the antiseptic action to the presence of acid phosphates which are removed in the salting.

E. le Cyon states that meat preserved by borax is not diminished in nourishing properties, and that it is more readily assimilated (B. C. 1879, 869), whereas Le Bon (*ibid.*) asserts that meat so preserved is useless as food. J. Forster concludes that the use of boric acid in preserving food is of questionable value, as it increases the secretion of bile and the excretion of albuminous matters (B. 16, 1,754). Gruber (B. C. 1880, 509) likewise states that the decomposition of albumen in animals is increased by borax. Vigier, on the contrary, concludes from a series of experiments on dogs and men that borax has no injurious effects, even in large doses. It appears to be slowly eliminated in the urine (Vigier, J. Ph. [5] 7, 301).

**Detection and determination of boron.** Boron almost always occurs in the form of boric acid. When the acid is in the free state it can readily be recognised by the green colour which it gives to the flame, and by its action upon turmeric.

The green colour imparted to flame is a very delicate test for boron (according to Merz, J. pr. Ch. 80, 487, 1 part in 1,400 may be detected by flame). It is, however, to be borne in mind that the salts of copper likewise colour flame green, as well as certain compounds of chlorine. When the boric acid is combined with a base the compound in the state of powder is decomposed by means of sulphuric acid, and the boric acid extracted by alcohol. Compounds not decomposed by sulphuric acid are fused with potash and digested with alcohol and sulphuric acid.

The presence of boron in minerals may be detected by mixing the mineral in powder with a flux containing 1 part fluorspar to  $4\frac{1}{2}$  parts hydrogen potassium sulphate, made into a paste with water, and heating the mixture in the inner blowpipe flame, when boron chloride is given off which tinges the flame green; or by

mixing the suspected substance with fluorspar and sand, moistening with concentrated sulphuric acid and passing the escaping gas through a tube drawn to a fine point into the non-luminous Bunsen flame which it colours green (Kämmerer, Fr. 1873, 376).

The spectrum of boron shows three bright lines in the green and one in the blue (Simmier, P. A. 155, 250). Hartley finds in the spectra of boric acid and borax the lines  $\lambda 3450.3$ ,  $\lambda 2497$ , and  $\lambda 2496.3$  which he considers characteristic of boron (Pr. 35, 301). For the measurement of the intensity of these bands v. Lecoq de Boisbaudran (C. R. 76, 883).

The quantitative estimation of boron is difficult, as all borates are soluble to some extent in water and alcohol, and boric acid cannot be heated without loss in contact with water.

One of the best methods of direct determination is to precipitate the boron as potassium borofluoride, which is quite insoluble in alcohol (Berzelius, Lehrbuch, 3 ed. 10, 84; Stromeyer, A. 100, 82).

In this method the solution must contain no other metal than potassium; all other bases must be removed and replaced by potash. Borates of the alkaline-earths, earth-metals, or heavy metals are fused with potassium carbonate and the mass digested with water; sodium borate is treated with alcohol and sulphuric acid, filtered, potash added to the solution, and the alcohol evaporated.

The potassium borate thus obtained is saturated with hydrofluosilicic acid and evaporated to dryness, the potassium fluoride removed from the residue by washing with potassium acetate and alcohol, and the potassium borofluoride dried at  $100^\circ$  and weighed. 100 parts of the borofluoride correspond to 9.06 boron or 27.78 boric anhydride (Stromeyer, l.c.).

Another method consists in adding to the aqueous or alcoholic solution a weighed quantity of sodium carbonate, evaporating to dryness and igniting the residue in a covered crucible. The residue contains sodium carbonate and borate. As the quantity of sodium is known, the estimation of the carbonic acid is sufficient to determine the quantity of boric anhydride present (Rose, P. A. 80, 262; J. 1850, 588).

Boron may be estimated indirectly by digesting a weighed quantity of the finely divided compound in a platinum vessel with hydrofluoric acid, and then with concentrated sulphuric acid. On warming gently the boron present is expelled as fluoride, and after driving off the excess of sulphuric acid, the quantity of bases in the residue is determined. Their weight, deducted from the weight of the original substance, gives the quantity of boric anhydride.

Or, by treating the pulverised borate with strong oil of vitriol and alcohol, the boron may be driven off as ethyl borate.

When combined with potash or soda, boric acid may be determined by evaporating the solution of the previously weighed salt with hydrochloric acid, and determining the chlorine in the dry residue (Schweizer, M. N. G. Z. 1850, 1; Ph. C. 1850, 372; J. 1850, 590).

Or volumetrically by means of a standard solution of sulphuric acid. The solution is coloured with litmus, and the sulphuric acid

added cautiously from a burette till the wine-red colour first produced changes to bright red.

#### Separation of boron from other elements.

Boric acid can be separated from most bases by boiling or fusing the substance with potash or potassium carbonate. Those bases which are precipitated by sulphuretted hydrogen or ammonium sulphide are separated by these reagents, and the boric acid determined in the filtrate (Marignac, Fr. 1, 405).

Sulphuric acid is readily separated from boric acid by means of barium chloride; hydrochloric, bromic, and iodic acids by silver nitrate; and phosphoric acid by ammonia and magnesium sulphate. In the presence of *fluorine* the estimation of boron is more difficult. Borofluorides are heated with sulphuric acid and the residue of metallic sulphate is weighed; the boron and fluorine are together driven off as boron fluoride and hydrofluoric acid. Or the fluorine may be converted into calcium fluoride by means of calcium acetate (Stromeyer, A. 100, 82; J. 1856, 722).

To determine the quantity of water of crystallisation in these compounds, they are mixed with 6 parts lead oxide, covered with a layer of lead oxide, and heated. The loss of weight gives the water.

There are no exact methods for the estimation of boron in the presence of silicates.

If the silicate is decomposable by acids it is pulverised and heated with hydrochloric acid, diluted with water and filtered, the filtrate treated with ammonia and oxalic acid to remove alumina and lime, and evaporated on the water-bath. The residue is ignited in a covered crucible, and boric anhydride is left mixed with silica. The boric anhydride is dissolved out by water and the residual silica weighed.

In silicates undecomposed by acids, the mineral is treated first with hydrofluoric and then with sulphuric acid, whereby both boron and silicon escape, and the bases combine with sulphuric acid and are determined as sulphates.

In a second portion of the mineral the silica is determined by fusion with a mixture of sodium and potassium carbonates. The boric anhydride is determined by difference after the estimation of the bases and of silica (Rose, A. C., 2, 734).

Boron may also be estimated in silicoborates by fusing with potassium carbonate, dissolving in water, and precipitating the bulk of silica from the solution by means of ammonium chloride; the remainder, after the removal of ammonium carbonate, is precipitated by zinc oxide dissolved in ammonia. Bodowig proposes to omit the precipitation with zinc oxide and to estimate the small quantity of silica still remaining in the borate precipitate obtained subsequently (Fr. 1884, 143).

The estimation of water in boric acid is made according to Stolba's process by igniting with 4 parts of borax. Gilbert (D. P. J. 259, 383) finds this method inapplicable in the presence of sulphuric acid, and proposes moistening 1.5 grains quicklime with 10 c.c. water, mixing it with 2 grains boric acid, evaporating to dryness, igniting and weighing. The loss of weight gives the water.

A solution of borax produces no change of colour in solutions of helianthin, tropæolin, and

methyl orange, but a drop of hydrochloric acid immediately changes the yellow colour into red. Borax may thus be titrated by the stronger acids (A. Joly, C. R. 100, 103).

Guyard proposes the use of boric acid as a standard acid solution in alkalimetry, lumatin being used as the indicator (Guyard, Bl. [2] 40, 422).

For the estimation of boric acid in mineral waters, v. Fresenius (Fr. 25, 202).

To detect boric acid in milk, baryta is added to 100 c.c. of milk till alkaline. After incineration, the ash is dissolved in a little strong hydrochloric acid, evaporated to dryness, and a solution of turmeric with a drop of dilute hydrochloric acid added, and the solution evaporated on a water-bath. 0.001 per cent. boric acid gives a distinct colour to turmeric in this manner (S. C. I. 1887, 563).

#### BORO-NATRO-CALCITE. *Hydroboracite*,

*Hayesin*, or *tiza*, a native borate of lime and soda, known in commerce as 'borate of lime.'

**BOSCH.** An inferior butter formerly prepared in Holland. The term is now synonymous with margarine, *q. v.*

**BOSJEMANITE.** A manganese alum found near the Bosjeman river, S. Africa, and at Alum Point, Salt Lake, Utah.

**BOSTONITE.** *Canadian asbestos* (v. ASBESTOS).

#### BOSWELLIA THURIFERA, or GUGAL.

The gum of this plant (Order *Bursaceæ*) is used as an incense. It is often confounded with bdellium and olibanum (Dymock, Ph. [3] 7, 190).

**BOTALLACKITE.** An oxychloride of copper, found at Botallack Mine, in St. Just, Cornwall.

#### BOTANY BAY RESIN v. BALSAMS.

#### BOTRYOLITE v. CALCIUM.

**BOTTLE-NOSE OIL.** An oil obtained from the bottle-nosed whale, closely resembles sperm oil; its sp.gr. varies from 0.876 to 0.880 (Allen, S. C. I. 2, 53).

**BOTRYOGEN or RED VITRIOL.** A native ferros-ferric sulphate from Fahlun, Sweden, of sp.gr. 2.039. It is of a dark hyacinth red to ochre-yellow colour.

**BOUILLON NOIR.** *Ferric acetate* (v. ACETIC ACID).

**BOULANGERITE.** A tribasic sulphantimonite of lead found at Molières, France, in Lapland and other localities (v. ANTIMONY).

**BOU-NEFA.** The root bark of *Thapsia garanica*, an umbelliferous plant growing in the South of Europe and Algeria. It contains a resin used as a medicine in France.

**BOURBOULITE.** A native ferros-ferric sulphate found at Bourboule, Puy-de-Dôme.

**BOURNEENE or VALERENE.** A liquid hydrocarbon isomeric with oil of turpentine, secreted by the *Dryobalanops Camphora*, and holding in solution borneol or Borneo camphor. According to Wallach (A. 230, 225; C. J. [2] 50, 70) it is a mixture of the decomposition products of camphene.

**BOURNONITE.** A sulphide of antimony, lead, and copper, found in Cornwall, Devonshire, and in many of the mining districts of Europe. It contains, according to Rammelsberg:

S.	Sb.	Pb.	Cu.	As.	Fe.
19.77	24.34	42.88	13.06	—	—

Wait (C. N. 28, 271):

S.	Sh.	Pb.	Cu.	As.	Fe.
19-359	23-577	41-949	13-263	0-469	0-679

### BOVEY COAL v. FUEL.

**BRACKEBUSCHITE.** A mineral described by Rammelsberg containing 25-32  $V_2O_5$ , 0-18  $P_2O_5$ , 61-00 PbO, 1-29 ZnO, 4-77 MnO, 4-65 FeO, 0-42 CuO, and 2-03  $OH_2$  (J. M. 1881, 2 R. 330; C. J. 42, 150).

**BRAGA BEER.** A beer made from hops and malt in Russia. For details see Cech., D. P. J. 240, 235 a. C. J. 40, 857.

**BRAM'S POWDER.** An explosive consisting of 60 parts of a mixture of potassium chlorate, potassium nitrate, wood charcoal, and oak saw-dust saturated with 40 parts of trinitroglycerine (W. J. 22, 476).

**BRAN.** (*Son*, Fr.; *Kleie*, Ger.) The husky portion of ground wheat separated by the boulder from the flour. It is advantageously used by calico-printers in the clearing process, in which, by boiling in bran-water, the colouring matters adhering to the non-mordanted parts of madder-dyed goods, as well as the dun matters which cloud the mordanted portions, are removed. From experiments made by Koechlin-Schouch it seems that two bushels of coarse wheat bran boiled with twelve hectolitres of water sufficed to clear ten pieces of calico in from fifteen to thirty minutes. Rye bran is not so good, and barley bran is useless for this purpose.

Bran has little nutritive power, but it contains a ferment, cerealin, which possesses the power of quickly converting starch into dextrine and sugar. Mouriès found that 130 parts of wheaten bread containing bran easily diffused through 520 parts of water when triturated therewith and yielded 59-35 parts of soluble bran and 69-75 parts of insoluble matter, whereas the same quantity of bread not containing bran yielded only 9-03 soluble to 120-25 insoluble matter.

From experiments made in Germany it appears that bran mixed with meadow hay diminishes the digestibility of the protein contained in the latter (B. C. 12, 459; S. C. I. 3, 186).

**BRANDY** is a spirituous liquor, the product of the distillation of wine, possessing a peculiar aroma due to minute traces of ether and certain volatile oils. The greater quantity of brandy is manufactured in the departments of Charente, Charente Inférieure, Landes, Gers, and Lot et Garonne, of which districts Charente and Charente Inférieure produce the highest class, known as Cognac. But little brandy is distilled in Cognac itself, the greater part being produced on the brandy farms in the district. The brandy grape is a small white berry, and yields a very acid juice. As received from the farmers, the distilled spirit is about twenty over-proof; it is diluted and mixed in vats, coloured with caramel, filtered through paper pulp into storage vats, in which it is matured. It is also obtained, but of greatly inferior quality, from Portugal, Spain, and Italy. Each locality furnishes a spirit of characteristic *goût*, which is readily recognised by the connoisseur, the variation arising from the difference of the soils as well as from the materials used. Thus it is said that the brandy of the Moselle wine has a slaty taste, that of St. Pierre in Vivarais the aroma of the violet, and that of Holstein a flavour resembling the oil of amber.

The quantity of wine used in the process of manufacture is very great, the amount of brandy produced from a given measure being only 10 to 15 p.c. The grapes of the South excel those of the North in the production of alcohol in the ratio, as between the extreme limits of locality, of nearly two to one. The best brandy is prepared from white wines. If stored in oak casks it acquires a slightly yellow colour, and is known as 'pale' brandy; 'brown' brandy deriving its deeper colour from the use of caramel or burnt sugar. It is sold of various strengths, usually about 10 p.c. under-proof, and rarely exceeds proof strength, as, on account of its flavour depending on the volatile oils, it is but slightly rectified. Its constituents are alcohol and water with small quantities of acetic acid, acetic ether, ananthic ether, volatile oil, colouring matter, and tannin absorbed from the cask. The alcohol amounts to from 45 to 55 p.c.

Morin distilled 92 litres of pure Cognac, prepared in 1883 from Charente Inférieure wine in Claudon and Morin's apparatus. The first portion of the distillate contained the more volatile bodies, the second consisted of tolerably pure ethyl alcohol, the third, the higher boiling alcohols, &c. The residue, chiefly water, was tested for free acids, isobutylglycol and glycerol.

The first three portions were then fractionated, 5 litres of light alcohol, 55 litres of pure ethyl alcohol, and 3-5 litres of higher boiling compounds being obtained. The latter fraction smelt strongly of fusel oil, and possessed a burning taste. The water remaining behind was added to that already obtained. The fractions were then redistilled in Le Bel and Henninger's apparatus. The fusel oil portion, which after dehydration by potassium carbonate weighed 352 grams, gave:

	Grams
Water . . . . .	7
Ethyl alcohol . . . . .	130
Norm. propyl alcohol . . . . .	25
Isobutyl alcohol . . . . .	6
Amyl alcohol . . . . .	175
Furfural . . . . .	2
Wine oils . . . . .	7

The water contained a little acetic and butyric acids and a small quantity of a viscous liquid, which distilled undecomposed under diminished pressure, and appeared to consist of isobutyl alcohol and glycerol. The residue contained tannin, together with substances extracted from the wood.

In the following table: 1 shows the compounds contained in 100 litres of the Cognac; 2 shows the same obtained by the fermentation of 100 kilos. of sugar:—

	1 Grams	2 Grams
Aldehyde . . . . .	Trace	Trace
Ethyl alcohol . . . . .	59,837-0	50,615-0
Norm. propyl alcohol . . . . .	27-17	2-0
Isobutyl alcohol . . . . .	6-52	1-5
Amyl alcohol . . . . .	190-21	51-0
Furfural bases . . . . .	2-19	0-0
Wine oil . . . . .	7-61	2-0
Acetic acid . . . . .	Trace	"
Butyric acid . . . . .	Trace	"
Isobutyl glycol . . . . .	2-19	"
Glycerol . . . . .	4-38	"



Butyl alcohol was absent; furfural was detected directly by the addition of aniline to the Cognac, a red colouration being produced in the presence of acetic acid (E. C. Morin, C. R. 105, 1,019; S. C. I. 7, 224).

By the Sale of Food and Drugs Amendment Act of 1877 it is ordered that brandy must not be sold weaker than 25 p.c. under-proof; in France the usual retail strength is 18 p.c. to 20 p.c. under-proof, the spirit at that strength being known as *eau-de-vie à preuve de Hollande*. The addition of water to brandy destroys the fine aroma for which it is prized.

The imports of brandy into the United Kingdom were:—

	Gallons	Value
1882 . . .	2,160,809	£973,408
1883 . . .	2,210,987	1,014,583
1884 . . .	2,382,897	1,066,430
1885 . . .	2,780,122	1,243,916
1886 . . .	3,139,022	1,424,942
1887 . . .	2,830,916	1,317,976
1888 . . .	2,647,065	1,219,155

British brandy is a liquor devised by the distiller in imitation of the foreign spirit, and many formulæ exist for its manufacture. The following is Ure's receipt: 'Dilute the pure alcohol to the proof pitch and add to every hundred pounds weight of it from half a pound to a pound of argol—crude tartar—dissolved in water, some bruised French plums and a quart of good Cognac. Distil this mixture over a gentle fire in an alembic provided with an agitator. The addition of brandy and argol introduces ænanthic ether, and, if a little acetic ether be added to the distillate, the whole imparts the peculiar taste of genuine Cognac brandy. Colour with burnt sugar, if necessary, and add a little tannic acid to impart astringency.'

Cider brandy is manufactured in the United States and Canada from cider and perry.

Dantzie brandy is made from rye ground with the root of *Calamus aromaticus*.

Guernsey brandy is the spirit of beet root flavoured to resemble true brandy.

BRASS v. ZINC.

BRASSIL. A local name for iron pyrites.

BRAUNITE. Native sesquioxide of manganese, v. MANGANESE.

BRAZILETTO. An inferior kind of Brazil wood obtained from *Cesalpinia brasiliensis*, growing in the West Indies.

BRAZIL NUTS are the fruit of *Bertholletia excelsa* (Order Myrtaceæ); they yield an oil containing 74 p.c. of elaidin and 26 p.c. stearine. The inner bark of the tree is also an article of commerce, being used for caulking ships and barges. According to Corenwinder, the kernels in a fresh condition contain 8.00 p.c. water, 65.60 oil, 15.31 nitrogenous matters, 7.39 non-nitrogenous, and 3.70 ash (Ph. [4] 18, 14; v. also Caldwell, A. 98, 120).

BRAZILWOOD. This dyewood may be taken as the typical representative of the class known as the 'soluble redwoods.' The principal members of this class are: *Pernambuco-wood*, which consists of the heart wood of *Cesalpinia crista*, and is imported from Jamaica and Brazil; *Sapan-wood*, obtained from *C. sappan*, which is imported from Ceylon, Siam, Japan, and other Eastern countries; *Peachwood*, the product of

*C. echinata*, from Central America and the northern parts of South America; *Limarwood*, a variety of sapan or peachwood, imported from Peru.

All these dyewoods contain the same or a very similar colouring principle; the colours they produce with the different mordants and their general chemical characters are also similar.

The logs as imported are rasped to a coarse powder which is then moistened with water and left in large heaps to ferment for several weeks. This operation is performed in order to increase the colouring power of the wood, and it is considered by some that the fresh wood contains a glucoside which under the influence of fermentation is split up into useful colouring matter and glucose. Practical men assert that this 'ageing' process is necessary to cause the dye-wood to give the best results, but the subject requires further study to decide whether this is really the case or not, and, if it is, to ascertain the real cause of the improvement. Excessive and too prolonged fermentation must at all times be avoided, otherwise the colouring matter is destroyed.

The commercial preparations of Brazilwood known as Brazil-extract and Brazil-liquor are prepared by boiling the ground fresh wood with water, and evaporating the decoction thus obtained to various degrees of consistency, without access of air, or as rapidly and at as low a temperature as possible, e.g. in vacuum pans.

The colouring principle present in the fresh wood is called *brazilin*. It crystallises from alcohol in the form of dark-yellow rhombohedra  $C_{16}H_{14}O_5 + H_2O$ , and from water in the form of needles  $2C_{16}H_{14}O_5 + 3H_2O$ . In cold water it dissolves slowly, but very readily in hot water, alcohol, and ether. In caustic alkalis it dissolves with a deep crimson colour which is destroyed on the addition of zinc powder. By the action of nitric acid it yields tri-nitro-resorcinol, and submitted to dry distillation it gives resorcinol itself. Treated with hydriodic acid and phosphorus it yields an amorphous product, *brazinol*  $C_{16}H_{14}O_4$ , which on distillation with zinc powder yields a hydrocarbon  $C_{16}H_{14}$  or  $C_{16}H_{16}$ . Fused with caustic potash it yields resorcinol, acetic and formic acids.

Brazilin is evidently of a phenolic character and acts the part of a weak acid, giving soluble red-coloured salts with alkalis and variously coloured insoluble compounds with the earths and metallic oxides. For this reason it is useful as a dyestuff.

Impure brazilin is occasionally found as a brownish-red crystalline crust in casks of Brazil-extract which have been left standing for a long time. By washing with dilute hydrochloric acid to remove lime, decolourising with sulphurous acid, and crystallising from alcohol and water, pure brazilin is readily obtained. By a more tedious method it may also be prepared from the wood or the extract.

The true colouring matter of Brazilwood of immediate use to the dyer is *brazileïn*  $C_{16}H_{14}O_5$ , produced by the oxidation of brazilin in alkaline solution. Judging from its chemical behaviour it probably belongs to the phthaleïn group of

colouring matters. It may be prepared as a brown amorphous powder by drawing air through an ammoniacal solution of brazilin for a few hours and then precipitating with acetic acid. Crystallised from dilute acetic acid it has the appearance of a dark-brown, almost black, crystalline powder possessing a steel-grey metallic lustre. Under the microscope the crystals appear as minute rhombs. Brazilin is very difficultly soluble in water, alcohol, and ether, giving a brownish-yellow solution, but it is readily soluble in alkalis with a carmine-red colour. When dissolved in concentrated sulphuric acid and precipitated with water it yields a compound of the formula  $C_{10}H_{11}O_5.HSO_4$ . Heated to  $100^\circ C$ . in sealed tubes with hydrochloric acid it gives an analogous body  $C_{10}H_{11}O_5.Cl$ .

The great similarity of behaviour shown by brazilin and hæmatein (the colouring matter of logwood) shows that a very close relationship exists between the two.

During the 'ageing' of fresh Brazilwood the brazilin becomes largely if not entirely changed into brazilein, and it is very probable that the utility of the operation should be referred to this change rather than to those above-mentioned.

Although still used in calico-printing and in wool-dyeing, Brazilwood and its allies have lost much of their importance, chiefly because of the fugitive character of the colours they yield. In calico-printing, sapan liquor is employed for producing steam-reds and pinks, the mordant used being aluminium acetate or stannic oxalate, separate or combined, together with some oxidising agent, *e.g.* potassium chlorate or a copper salt. It also enters into the composition of steam chocolates and other steam colours in conjunction with other dyewood extracts. These woods have also been much used in the past along with garancine in dyeing the reds, chocolates, and other colours of cheap prints.

In wool-dyeing these woods have been applied for the purpose of dyeing reds and various shades of claret and brown, the wool being previously mordanted with alum and cream of tartar or oxalic acid, or with potassium bichromate, in which case other dyewoods, *e.g.* logwood and old fustic are dyed in addition. The colours produced by this method are now seldom used.

In cotton-dyeing, peachwood-red was formerly obtained by first preparing the cotton with tannin matter, then mordanting with a stannic salt, and finally dyeing with peachwood, sapanwood, &c. Browns were obtained by the use of logwood in addition, with or without a final passage through a ferric salt solution (nitrate of iron). These colours are now replaced by others obtained from coal-tar.

In silk-dyeing these woods have also been entirely replaced by coal-tar colours. Formerly they were used in conjunction with aluminium and tin mordants for low-class pinks, or for purples if logwood was applied at the same time.

References.—Bolley, J. p. 153, 351; Reim, B. 4, 334; E. Kopp, B. 6, 447; Benedict, A. 178, 101; Liebermann and Burg, B. 9, 1885; Hummel and Perkin, B. 15, 2337; Chevreul, A. Ch. [2] 82, p. 53-126; Leçons Chim. teint. ii.; Journ.

Chim. Méd. 6, 157; Wiedemann, B. 17, 194; Buchka and Erek, B. 18, 1138; Dralle, B. 17, 372; Halberstadt and Reis, B. 14, 611; Schützenberger and Paraf, Bull. Mulhouse, 31, 50; A. [1] 6, 17; 12, 221; 20, 387; 66, 225; A. [2] 17, 323; 19, 283; D. P. J. 25, 80; 52, 146; 54, 373; 93, 111, 116. J. J. H.

#### BRAZILIAN ANIME *v.* OLEO-RESINS.

**BRAZILIN** and **BRAZILEIN** *v.* BRAZILWOOD.

**BREAD.** The dough or paste made by the mixture of the flour of grain with water and afterwards baked, forms the article of food which we know by this name. The simplest and most primitive method of bread-making consisted merely in an operation conforming strictly to this definition, and it survives still in the Passover-cakes of the Jews and in the 'damper' of the Australian settler, which are examples of what we know as unleavened or unfermented bread. It is, however, the almost universal custom to introduce into the kneaded mass of dough an amount of carbonic acid gas sufficient to give a spongy texture to it, either, (1) by the fermentative action of leaven or of yeast, or (2) by causing an acid to react on bicarbonate of soda mixed with the flour, or (3) by directly injecting the gas. The mechanical result of this operation is the creation of innumerable vesicles or cells within the dough which are subsequently distended by heat, the whole mass being encased in the baking within the crust of dextrin formed by the action of heat upon the starch. The result of this action is the formation of a soft spongy crumb, instead of a heavy and sodden mass, and the constituents of the flour are thereby so altered both chemically and physically, that the bread may not only be more readily broken up by the action of the teeth but also more easily permeated by the saliva and gastric juice, and thus made more readily digestible. Leavening (Lat. *levo*, to raise), has been practised from time immemorial in the East; from the Egyptians it passed to the Greeks and thence to the Romans, whose conquests and colonies extended the art. It consisted in the first instance probably in a natural fermentation of the dough by leaving it to become sour; but to hasten the process it became usual to add to new dough a portion of old fermented paste or 'leaven.' More recently 'yeasts' have been substituted for the piece of leaven as a means of propagating the fermenting principle. These are of various substances and origin, such as an infusion of hops and malt, brewers' yeast, and pressed or German yeast. It is this last preparation which finds most favour with the modern baker because its greater activity curtails the time occupied in the 'rising' of the dough. It is, however, his practice to make a ferment of potatoes, technically called by him 'fruit' since the potato being rich in soluble starch of large grain sets up a livelier fermentation. For this purpose the best potatoes available are selected, and for every sack of 280 lbs. of flour 6 to 8 lbs. are employed. After having been carefully washed and boiled they are 'mashed' into a paste and cold water added until the heat of the mash stands at about  $85^\circ$  Fahr. To this is added a quantity of flour varying according to the practice of the baker from 2 to 12 lbs. and

scalded in boiling water together with a quart or rather more of yeast. This mixture, forming a thin paste, is now left to ferment vigorously for about five hours before the flour in bulk is added.

The action of yeast is caused by minute organisms (*Saccharomyces cerevisia*) which propagate at the expense of the substances on which they feed. It is quite possible to have some kind of leaven introduced into dough by simply exposing it to the air to be acted upon

by whatever chance organisms may happen to fall upon it. These organisms in leavening dough all convert starch into carbonic acid and water if exposed to the air, and so act upon saccharine matter as to convert it mainly into alcohol and carbonic acid (v. FERMENTATION). The action of yeast on flour and the process of panification generally is materially affected by the nature and amount of the various constituents of the grain of cereals. The following table gives the

*Average Composition of the Flour of Cereals (Lawes & Gilbert).*

—	Old Wheat	Barley	Oats	Rye	Maize	Rice
Water . . . .	11.1	12.0	14.2	14.3	11.5	10.8
Starch . . . .	62.3	52.7	56.1	51.9	54.8	78.8
Fat . . . . .	1.2	2.6	4.6	2.0	4.7	0.1
Cellulose . . . .	8.3	11.5	1.0	6.4	14.9	0.2
Gum and Sugar . . . .	3.8	4.2	5.7	11.3	2.9	1.6
Albuminoids . . . .	10.9	13.2	16.0	8.8	8.9	7.2
Ash . . . . .	1.6	2.8	2.2	1.8	1.6	0.9
Loss &c. . . . .	0.8	1.0	0.2	0.5	0.7	0.4
	100.0	100.0	100.0	100.0	100.0	100.0

The relative proportion of the proximate constituents of cereal grains varies very greatly with the variety of the species, the nature of the soil, and the conditions of growth and of harvesting (v. CEREALS). These constituents may for dietetic purposes be divided into three main groups—(1) The carbohydrates, *i.e.* the starches, sugars, and gums; (2) the albuminoids or nitrogenous matters; (3) the ash or mineral matters. The gluten is the main flesh-forming constituent of flour, and consists chiefly of vegetable fibrin in union with a nitrogenous substance called *gliadin* which gives to the dough its characteristic adhesiveness and power of rising into a spongy mass when penetrated by the carbonic acid. Other cereal grains contain but little gliadin and therefore yield doughs which lack the peculiar lightness and porosity of that made from wheaten flour. Hence bread is most frequently made from the flour of wheat and rye, the other cereals being used to a comparatively small extent for this purpose. The character of the bread depends on the quality and nature of the flour, and the manner in which it is leavened or fermented. The characteristic action of leaven is well seen in the manufacture of the *Schwarzbrod* or black bread of Germany.

The fermenting mass when added to freshly made dough converts a portion of the starch into maltose, which together with the sugar present in the flour is transformed partly into alcohol and carbonic acid and partly into lactic, acetic, and butyric acids which act as solvents for certain of the proteids contained in the flour. These acids also appear to convert the gluten into a soluble substance which rapidly darkens on exposure to the air, whereby the bread acquires its peculiar colour.

Old leaven runs ultimately into the acid fermentation alone, and hence the colour of the bread is materially affected by the age of the leaven from which it is made. It is, however, possible to make the finest wheaten bread by

means of leaven, and such bread is so made by the Parisian bakers. Their practice in the preparation of the leaven consists in a series of stages (*levain de chef, levain de première, levain de seconde, and levain de tout point*), by which, starting with a piece of dough put away from a previous baking, and adding at intervals more and more flour and water, the required quantity is leavened. From this istaken a half, which when baked yields a dark sour bread; the remainder being again mixed with a quantity of flour, produces a whiter and less sour dough, a portion of which is baked and the residue once more added to fresh flour. By this means the last mixing produces bread which in point of whiteness leaves nothing to be desired. The action of yeast transforms the starch in part into sugar (or more properly glucose), alcohol, and carbonic acid gas, and it is when this last has sufficiently permeated the mass of dough, made tenacious by the gliadin of the gluten, and detained in bubbles or cells, that the loaf is put in the oven where the fermentative process is arrested. Here a still further expansion of the gas is caused by the increased heat, until the walls of the cells and the outside crust are fixed by the hardening effect of the baking. But besides the transformation of the sugar into carbonic acid an action is set up in the nitrogenous substances whereby they act as ferments to the starch, converting it by the action of diastase into dextrin and sugar, and sometimes into lactic acid. This may be carried to such an excess as to be detrimental to the bread, and is always a cause of a dark, heavy, tenacious, and more or less saccharine loaf. Wheat harvested in bad condition or exposed during harvesting to much wet weather yields flour predisposed to the diastatic state whereby the starch cells burst and become converted into dextrin and maltose. In bread of the best description it will be found that the starch has experienced very little alteration.



The brown colour of bread made from flour containing bran is mainly due to the conversion of the starch into dextrin and sugar by the agency of the albuminous matter of bran, the *cerealin* of Mège-Mouriès, which seems to be identical with diastase, or has at least the same activity in inducing the transformation. But since bran contains a larger proportion of potash and phosphoric acid than the interior of the kernel of wheat, a public demand has arisen for bread more or less composed of the outer husk, and various expedients are resorted to by the baker to comply with this want, such as hastening the fermenting process, or adding the bran after the flour is almost completely fermented and thereby isolating it as far as possible from the operation. Another device is the use of hydrochloric acid and bicarbonate of soda for raising the flour; another, again, is the employment of Dr. Daughlish's plan of 'aeration.' The opponents to the use of bran allege a physical dietetic objection to it, inasmuch as the husk being presented in a hard, fibrous condition, the gastric juices are unable to cope with it, and an irritant action is induced which is injurious, especially to persons of weak digestion. A patent has been granted to Mr. R. Smith of Stoke-on-Trent for a process which consists in the removal of the germ from the wheat, the destruction of its active injurious properties, and its restoration to the flour. After the grain of wheat has been broken up and the germ thereby exposed, superheated steam is allowed to come in contact with it. It is claimed that by this means the heated germ has lost its injurious power without its nutritive power being impaired, and that on its being mingled with flour it imparts to the bread a pleasant, malt-like, nutty flavour and aroma. It has long been known to bakers that the injurious action of the diastase on the starch during panification may be prevented by the action of alum, lime, zinc sulphate, copper sulphate, and other substances. Alum is mainly used in this country, whereas zinc and copper sulphates are employed in France and Belgium. There is no doubt that the employment of these substances enables flours of inferior quality to be worked up into white, elastic, crumbly bread which would otherwise be dark-coloured and sodden. A very small quantity of alum in bread has probably very little if any injurious action on the digestive functions, and it certainly permits of many flours being used for bread-making which would otherwise be employed only for the manufacture of dextrin. Moreover, alum by retarding the transformation of starch into lactic acid prevents the bread from turning sour. The statement that the addition of alum causes bread to retain a larger quantity of water than it otherwise would do has been disproved by Odling.

The use of lime in preventing the conversion of starch into dextrin and lactic acid appears to have been first suggested by Liebig. It seems to be quite as efficacious as alum, whilst it exercises a less retarding influence on the process of fermentation, and is, moreover, free from any injurious action as an astringent. Since the fermentative action is attended with the loss of a certain proportion of the nutritive alimentary matter of the flour, amounting to from 2 to 4 p.c., various substitutes for yeast have been

proposed from time to time, as for example, ammonium sesquicarbonate or an admixture of hydrochloric or tartaric acids with sodium bicarbonate or chalk, in order to liberate carbonic acid within the dough. Horsford's baking powder, which has been extensively used, consists of acid calcium and magnesium phosphate added to a mixture of sodium bicarbonate and potassium chloride, the two preparations being worked separately into the dough. By the mutual action of these salts, common salt, neutral phosphates of the alkalis and alkaline earths, and free carbonic acid are produced. The formation of these phosphates has been generally considered to add to the alimentary value of the bread, although the experiments of Voit and Meyer have failed to substantiate the supposition (*v.* BAKING POWDERS).

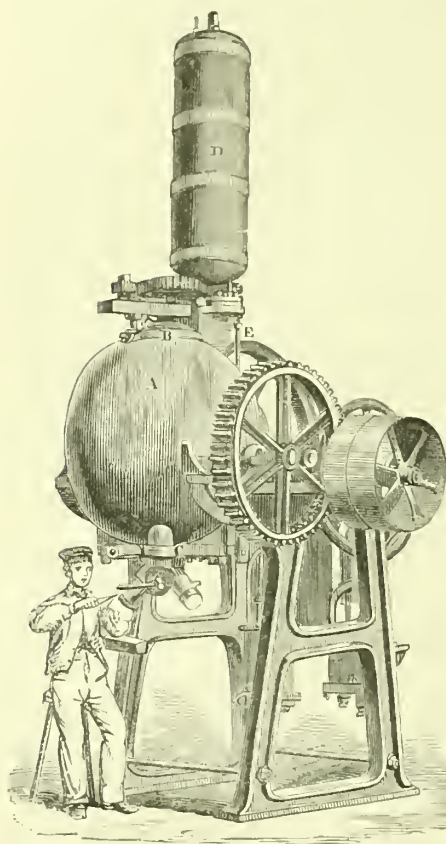
The injection of carbonic acid gas into the dough by mechanical means was originated by Dr. Daughlish in 1859, the produce being known as 'aerated bread.'

The following description of the method of preparing aerated bread is taken from Watts's Dictionary of Chemistry, 1st ed 1, 660:—Carbonic acid gas produced from chalk either by the action of dilute sulphuric acid or by ignition, and stored in an ordinary gas-holder, is pumped therefrom into a cylindrical vessel containing water, whereby the water becomes charged with the gas. This carbonic acid water is mixed under pressure with the flour, and the resulting dough, which becomes vesicular on the removal of the pressure, is divided into loaves and baked. This process, which was invented and patented by Dr. Daughlish, has been carried out on a large scale in London and other places.

The following is a description of the apparatus: A is the mixer or vessel in which the flour, water, and salt are mixed together. It consists of a very strong iron spheroidal vessel with an internal capacity of 17 to 20 cubic feet. It has an opening B at the top, to which an air-tight cover is fitted, and the means of closing it to resist considerable pressure. There is also a corresponding opening C at the bottom, large enough for a man-hole, and also closed by a lid, to which is attached the apparatus for drawing off the dough through suitable mouth-pieces in a continuous stream, which is cut into pieces by a boy, and received into boxes or baskets to be conveyed to the oven. Through the centre of the mixer, a shaft passes furnished with stuffing-boxes, to prevent the escape of compressed gas, and in this shaft suitable mixing arms are fixed. By means of the necessary gearing this shaft is made to rotate by steam-power. D is a copper water-vessel having communication with the mixer from the bottom by means of a valve, and from the top by means of a pipe passing up inside the water-vessel. This water-vessel has also communication with a pair of condensing pumps, which are fixed in the same frame behind the mixer and are worked by a steam engine. The communication is by means of the pipe E, which terminates within the water-vessel by a rose perforated with minute holes.

To work the apparatus, the top cover B of the mixer is opened, and about 560 lbs. of flour are shot into it by means of a hopper and shoot

connecting with the floor above; water, to the amount of thirty gallons or so, is drawn into the water-vessel from a cistern above, and the whole is then closed, after adding to the flour the necessary quantity of salt. The air is then removed from the apparatus by a suitable pump, and carbonic acid is pumped by the condensing pump from a gas-holder in which it is stored, until it is condensed to about seven atmospheres. This condensed gas being dispersed by the rose at the bottom of the water-vessel, passes in minute streams through the water, and as the density within increases, the water absorbs the gas in



proportion, that which is not absorbed passing down the internal pipe from the top of the water-vessel into the mixer, so that the density within that vessel is kept in equilibrium with that in the water-vessel. When the proper density is attained, the valve at the bottom of the water-vessel is opened, when the water falls upon the flour, after which the mixing arms are set to work, and in about six minutes the dough is thoroughly formed. It is allowed to subside for a minute and is then drawn off through the bottom apparatus, being forced through it by the elastic force of the gas within. On escaping from the condensed atmosphere in the mixer, the dough immediately assumes the vesicular form and texture, and is ready to be baked.

The carbonic acid is obtained by acting on whiting or ground chalk with sulphuric acid; it comes off perfectly pure, and, being kept over water, is thoroughly washed. It takes about 20 cubic feet of carbonic acid at the ordinary pressure to prepare dough from 280 lbs. of flour, about 11 cubic feet being incorporated with the dough, the remaining 9 cubic feet being wasted in the operation of drawing the dough off, and in other ways: 7 lbs. of sulphuric acid of sp.gr. 1.848 give, in practical working, 21 cubic feet of carbonic acid from 10 lbs. of carbonate of lime. The gas which is left in the apparatus after the dough is discharged is returned to the gas-holder for further use.

The advantages of the system are stated to be:

- '1. It does away entirely with fermentation and with all those chemical changes in the constituents of the flour which are consequent upon it.
- '2. It avoids the loss consequent upon the decomposition of starch or glucose consumed in the process of fermentation, estimated at about from 3 to 6 p.c.
- '3. It reduces the time requisite to prepare a batch of dough for the oven, from a period of from eight to twelve hours to less than thirty minutes.
- '4. Its results are absolutely certain and uniform.
- '5. It does away with the necessity for the use of alum with poor flour, and the temptation which bakers are under to use it with all.
- '6. It has the recommendation of absolute and entire cleanliness, the human hand not touching the dough or the bread from the beginning to the end.
- '7. The journeymen are relieved from a circumstance most injurious to their health—that of inhaling the flour-dust in the process of kneading.
- '8. It will produce a healthier condition of the baking trade, and thereby diminish to a great extent the inducements which lead to the extensive system of fraud now practised upon the public by the production of adulterated and inferior bread.
- '9. It will effect an immense saving in the material from another source, namely the sacrifice of at least 10 p.c. in the nutritive portion of the grain, hitherto lost as human food by the method of grinding and dressing necessary in the preparation of flour for making white bread by fermentation.
- '10. Together with the preservation of this large proportion of the entire quantity of wheat converted into flour, there is also the important result of the proportion preserved (the cerealin) being a most powerful agent in promoting the easy and healthy digestion of food.'

The amount of bread yielded by a given weight of flour depends upon the nature of the flour and the form of the loaf. The smaller the loaf, or in other words the greater the proportion of crust to crumb, the greater is the loss. According to Heeren 100 lbs. of wheaten flour as a rule yield about 125 lbs. of white bread, and 100 lbs. of rye flour give 131 lbs. black bread.

The proximate composition of bread differs in many respects from that of the flour from

which it is made. Much of the starch is changed into dextrin and sugar, and in the crust is converted into empyreumatic matter (*assamar*). The greater part of the carbonic acid and alcohol formed during the fermentation is dissipated during the baking, although fresh bread still retains from 0.245 to 0.399 p.c. of alcohol (Bolas). (Odling estimated that the amount of alcohol thus evolved in London alone

was in 1858 equal to 300,000 gallons of spirits.) A small portion of the sugar is converted into lactic acid and some part of the alcohol into acetic acid which give to an aqueous infusion of bread an acid reaction. The proteids and soluble albuminoids are but slightly altered beyond being made partially insoluble by the heat. The general composition of bread is very variable, as is shown by the following results of analyses by König:—

	Water	Albuminoids	Fat	Sugar	Non-nitrogenous	Cellulose	Ash
Wheaten bread.							
Minimum . . .	26.39	4.81	0.10	0.82	38.93	0.33	0.84
Maximum . . .	47.90	8.69	1.00	4.47	62.98	0.90	1.40
Mean (best quality)	38.51	6.82	0.77	2.37	40.97	0.38	1.18
„ (coarse „)	41.02	6.23	0.22	2.13	48.69	0.62	1.09
Rye bread.							
Minimum . . .	35.49	3.49	0.10	1.23	32.82	0.29	0.86
Maximum . . .	48.57	9.22	0.83	4.55	51.13	0.39	3.08
Mean . . .	44.02	6.02	0.48	2.54	45.33	0.30	1.31

The difference between fresh and stale bread is not due, as generally supposed, to loss of moisture, but, appears to be caused by the gradual combination of the water with the starch. This combination is readily broken up by heat, which serves to explain why stale bread acquires the appearance and properties of new bread on being heated. (Compare Balland, J. Ph. 1885, 5, 12 *et seq.*) For a description of bread-making machinery and of various forms of ovens *v.* Ure's Dictionary; Ency. Brit. 9th ed., art. BAKING; Muspratt's Chemistry.

**BREAN** *v.* OLEO-RESINS.

**BREEZES.** (*Braise*, Fr.) The dust of coke or charcoal. The coke burner applies this term to the small residual coke obtained in coke burning. The sifted ashes removed from houses is called 'breeze,' and sold under that name to brickmakers and others. An arrangement for burning breeze is described in S. C. I. 5, 425.

**BREIDIN** *v.* OLEO-RESINS.

**BREIN** *v.* OLEO-RESINS.

**BREMEN BLUE** and **BREMEN GREEN.**

Pigments containing a basic copper carbonate with alumina and calcium carbonate.

**BREWING.** 1. *Introduction.* Beer (Fr. *bière*; Ger. *bier*) may be defined as a spirituous liquor made from any farinaceous grain, but preferably from barley, which is first caused to germinate, then ground and mashed with hot water whereby its fermentable substance is extracted. This wort, as it is then termed, is next boiled up with hops, which besides imparting an agreeable bitterness to it, precipitate certain albuminous bodies. The liquor drained off from the hops is cooled down, yeast added and fermentation set up. After the liquor has ceased fermenting it is freed from the yeast, run off into casks and sent away for consumption. It may be of different degrees of strength and colour according to the quantity and nature of the ingredients employed in its manufacture; thus we may have mild ale, strong ale, light dinner ale, pale ale, bitter beer, porter, and stout.

2. The ingredients used in the manufacture of English beer are water, barley malt, malt

adjuncts such as maize, rice, sugar, glucose, saccharum, &c., hops and yeast.

3. **Water.** The principal seat of the brewing trade in Great Britain is Burton-on-Trent, which owes its great commercial prosperity in this branch of chemical industry to a certain chemical property possessed by the waters of this locality which render them pre-eminently suitable for brewing purposes. This property is nothing more or less than the presence of calcium sulphate in large quantities in these waters, derived from the deposits of gypsum contained in the Keuper marls of the district.

4. The waters supplying the Burton breweries are derived from two sources: 1. from the valley gravels (shallow wells), and 2. from the red marls and water stones of the new red sandstone formation, obtained by artesian borings.

The following analyses of these waters may be regarded as typical. No. 1 sample, from a well sunk to the depth of 29 feet in the valley gravels, very fairly represents the composition of the mineral constituents of the older and shallow wells of the district, in which the sulphates of lime and magnesia are partially replaced by carbonate of the same metals due to the percolation of rain water charged with carbonic acid gas

TABLE I.

	In grains per Imperial gallon	
	Shallow well	Deep well
Calcium sulphate . .	25.480	70.994
Magnesium sulphate .	Absent	12.600
Calcium carbonate . .	18.060	9.046
Magnesium carbonate .	9.100	5.880
Potassium sulphate . .	2.275	0.966
Sodium sulphate . . .	7.630	13.300
Sodium chloride . . .	10.010	9.120
Ferric oxide . . . .	0.837	1.130
Silica . . . . .	0.840	1.120
Total mineral matter	74.232	124.206



through the gravel bed. No. 2, from an artesian boring sunk *through* the gravel and *into* the underlying red marl to a total depth of 97 feet, may be taken as a type of the deep wells of the district.

It will be seen from these tables that the chief characteristics of both waters are the large quantities they contain of certain mineral salts, but especially of gypsum. The brewing excellences of the Burton water are supposed to arise partly from its freedom from organic matter, but mainly from the circumstance that the mineral constituents are of such a nature as to favour the extraction of all the alcoholic principle of the malt without at the same time taking up the colouring matter; hence the Burton water is peculiarly fitted for brewing those various qualities of pale ale for which the town has been so long celebrated.

5. From this it will be seen that no matter how pure a water may appear to be by chemical analysis, it by no means follows that such a water would be the most suitable for brewing purposes or produce the best beer. Certainly it is advisable that a brewing water should contain in solution as little as possible of those matters which are derived from the decomposition of organic substances and especially those of animal origin, but at the same time unless it holds in solution certain mineral salts in given quantity it is comparatively useless for brewing purposes. Of course, the presence or absence of such salts

will entirely depend on the geological nature of the various strata throughout the country; thus, whilst the Burton waters are highly saline, the waters of Thames Valley deep wells are strongly alkaline, whilst in Wales, Cornwall, and Cumberland we find waters containing little or almost no solid matter in solution, or frequently highly peaty in character and containing as much as four grains per gallon of organic matter, but entirely of vegetable origin.

6. For purposes of convenience all waters may be classified as follows:

I. Alkaline, from the chalk, the predominating mineral constituents being potassium and sodium carbonates.

II. Calcareous, from the carboniferous and liassic limestones, the predominating constituents being calcium and magnesium carbonates.

III. Saline (a) from the new red sandstone, the predominating constituents being calcium and magnesium sulphates.

IV. Saline (b) from wells near the coast, the predominating constituent being sodium chloride.

V. Peaty, containing principally vegetable organic matter.

VI. Waters from the primary rocks, containing very little or only traces of mineral matters in solution.

VII. Waters of no distinctive character.

The following analyses may be given as examples of these various types of water:—

TABLE II.

	1	2	3	4	5	6	7	8	9
	Alkaline	Calcareous	Saline (a)	Saline (b)	Peaty	Primary rocks	No distinctive character	Mild ale	Pale ale
Calcium sulphate . . . .	—	0.69	70.99	6.39	2.25	0.22	1.53	25	40
Magnesium sulphate . . . .	—	—	12.60	0.18	2.77	—	—	5	8
Calcium carbonate . . . .	3.25	13.87	9.04	—	—	—	1.27	15	15
Magnesium carbonate . . . .	1.47	0.44	5.88	4.87	0.87	—	1.35	—	—
Potassium sulphate . . . .	7.31	—	.97	—	—	—	—	5	10
Sodium sulphate . . . .	—	—	13.30	—	—	—	—	—	—
Potassium carbonate . . . .	9.58	—	—	—	—	—	—	—	—
Sodium carbonate . . . .	6.61	—	—	—	—	—	—	—	—
Calcium and magnesium nitrates	—	—	—	—	—	—	.46	—	—
Potassium nitrate . . . .	—	—	—	—	0.68	—	.27	—	—
Magnesium chloride . . . .	—	—	—	—	—	—	—	3	5
Potassium chloride . . . .	—	—	—	—	0.79	—	.48	—	—
Sodium chloride . . . .	14.99	1.73	9.17	59.67	1.45	1.53	1.76	20	30
Oxides of iron and alumina . .	0.03	0.45	1.13	0.35	0.84	—	.10	—	—
Silica . . . .	0.38	—	1.12	0.28	0.49	0.10	.33	—	—
Total mineral matters . . . .	43.62	17.18	124.20	72.04	10.14	2.15	7.55	—	—

7. From the foregoing it will be seen that for the brewing of ales the water to be most preferred is undoubtedly that of the saline type, and if it should fall to the brewer's lot not to possess such a water supply he must render the one he has available by the addition of certain saline ingredients suitable for his purpose. In order to do this a complete analysis of the mineral constituents of the water must first be made, and then sulphates of lime, magnesia, and potash, and sodium chloride added in such proportions as to bring the mineral constituents up to the required standard, either to that shown in column 8 if intended for mild ales, or to that of column 9 if intended for pale ales.

In the case of neutral waters, the necessary mineral salts are simply added to the water in the given proportions, but if the water be alka-

line, the alkaline carbonates must first be destroyed before further treatment. An essential condition in hardening a water with calcium sulphate is that the process shall be regular, and the best method of getting the gypsum into solution is decidedly by passing the water as it issues from the supply tap or storage cistern through a tank filled to three-quarters its depth with gypsum stones about the size of a hen's egg. The method of procedure is shown below:

A is a wooden round, having a perforated false bottom B, on which the gypsum stones rest; C, water inlet from main or cistern; D, indicating valve; E, waste-pipe having a fall of 30 feet for washing out; F, wash-out valve; G, overflow pipe to liquor tank. The valve D being opened to the requisite degree, and F closed, the water enters at C, percolates through the

gypsum in A, and flows over through the pipe G into a liquor tank. The rate of flow of the water which determines the amount of gypsum to be taken up is regulated by the valve D. The size

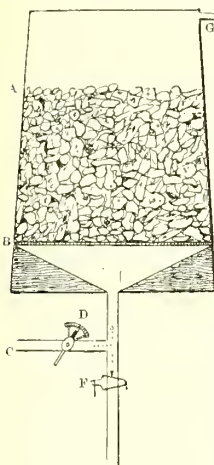


FIG. 1.

of gypsum tank and the speed at which the water passes through will determine the quantity taken up. As a rule, a tank capable of holding about a ton of gypsum and with a water of the composition of No. 2 flowing through it at the rate of three barrels per minute, takes up about twenty grains per gallon of calcium sulphate. Fresh gypsum must be added daily so as to keep the depth of layer of gypsum as regular as possible. To prevent an accumulation of slimy deposit which always takes place to a greater or less extent, the gypsum in the tank should be thoroughly well washed every other week; this may be done by closing D and opening F, then turning water on at the top of B, this passing through such a length of pipe as E causes a certain amount of suction which produces the desired cleansing effect. Some brewers recommend the addition of the gypsum in a state of fine powder either to the hot liquor tank before, during, or after the heating of the water preparatory to mashing, others sprinkle it over the grist as it runs into the mash tun, whilst others again add it to the wort as it is boiling up in the copper. None of these methods can be recommended, as in no one case will the *whole* of the gypsum be taken into solution, hence the brewing liquor will, according to varying circumstances, contain different quantities of calcium sulphate, but always less than is really required. After the whole of the water required for mashing and sparging has run through the gypsum tank into the hot liquor back, then the other salts are added. This may be most conveniently accomplished by the use of kainite and common salt in such proportions as chemical analysis may point out to be necessary. For instance, let us take water No. 4; here it was found that by passing the natural water through about a ton of gypsum at a speed of three barrels per minute, twenty grains per gallon of calcium sulphate were taken into solution; kainite at the rate of 2 oz. per barrel and common salt 1 oz. per barrel were next added; the mineral constituents of this water had then the composition shown in column II.

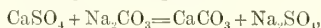
On referring to our table of typical analyses it will be seen that this water is of the mild ale

type. To render it suitable for brewing pale ales, the water must be run at less speed through the gypsum tank so as to increase the calcium sulphate, and further quantities of kainite and common salt must be added as shown in column III.

TABLE III.

	I.	II.	III.
Calcium sulphate . .	0.69	20.69	35.69
Magnesium sulphate .	None	4.41	8.82
Calcium carbonate . .	13.87	13.87	13.87
Magnesium carbonate .	0.44	0.44	0.44
Potassium sulphate . .	None	5.23	10.46
Magnesium chloride . .	None	2.88	5.76
Sodium chloride . . .	1.73	18.35	32.96
Oxides of iron and alumina . . . . .	0.45	0.45	0.45
Silica . . . . .	None	—	—
Total solid matters . .	17.18	66.32	108.45

In the case of alkaline waters, as soon as the calcium sulphate enters into solution a distinct chemical action between it and the alkaline carbonates takes place, calcium carbonate being formed, and sulphates of the alkalis. It is generally assumed that this reaction takes place according to the equation



but this has been proved not to be the case. From numerous experiments made to determine this point, the following conclusions were arrived at:

a. If the quantity of calcium sulphate added be less than the quantities of alkaline carbonates present, then *all* the calcium sulphate is at once converted into calcium carbonate, and an equivalent quantity of alkaline carbonates is converted into alkaline sulphates.

b. If the quantity of calcium sulphate added be equivalent to the quantity of alkaline carbonates present, then only about three-fourths of the calcium sulphate is converted into calcium carbonate, and an equivalent quantity, that is to say, three-fourths of the alkaline carbonates present, are converted into alkaline sulphates. As we increase the calcium sulphate, the alkaline carbonates decrease, until when we add double the equivalent of calcium sulphate nearly the whole of the alkaline carbonates are converted into alkaline sulphates.

c. The last portions of the alkaline carbonates seem to be very persistent, for not until we increase the quantity of calcium sulphate to nearly three times the quantity of alkaline carbonates originally present do we find that the last traces of these substances finally disappear. These are the results of numerous experiments carried out by the author both in the laboratory and on the large scale in breweries where the deep well water supply was highly alkaline in character, and it was found that the results obtained on the large scale fully confirmed those arrived at in the laboratory.

The following analyses of an alkaline water before and after treatment with gypsum will make this more clear :

Analysis of kainite :

Magnesium sulphate . . . . .	17.92
Potassium sulphate . . . . .	24.79
Magnesium chloride . . . . .	12.35
Sodium chloride . . . . .	29.20
Water . . . . .	15.74

TABLE IV.

*Analysis of an alkaline water before and after treatment.*

	1 Before	2 After gypsum	3 After gypsum	4 After gypsum and MgCl <sub>2</sub>
Calcium sulphate . . .	absent	27.92	35.62	44.95
Magnesium sulphate . . .	absent	absent	absent	14.39=11.39 (MgCl <sub>2</sub> )
Calcium carbonate . . .	3.25	13.44	16.42	16.42
Magnesium carbonate . . .	1.47	1.47	1.47	1.47
Potassium sulphate . . .	7.31	14.21	19.39	9.39
Sodium sulphate . . .	absent	8.86	8.86	absent
Potassium carbonate . . .	9.58	4.11	absent	absent
Sodium carbonate . . .	6.61	absent	absent	absent
Potassium chloride . . .	absent	absent	absent	8.56
Sodium chloride . . .	14.99	14.99	14.99	22.29
Oxides of iron and aluminium . .	0.03	0.03	0.03	0.03
Silica . . . . .	0.38	0.38	0.38	0.38
Total mineral matter . .	43.62	85.41	97.16	117.88

Column 1 shows the composition of the mineral constituents of the natural water.

Column 2, the same water after 41.79 grains per gallon of gypsum had been added, but the water was found to be still alkaline, and not until 53.54 grains of gypsum were added did the alkalinity disappear.

Column 4 gives the composition of the mineral constituents after the addition of a further quantity of gypsum, and 11.39 grains of magnesium chloride to decompose the excess of alkaline sulphates.

The ales brewed with this water after the above treatment were found to give every satisfaction, and to compare very favourably with the best Burton pale ales.

It will be noted that the alkaline sulphates originally present in the water are considerably increased by such treatment, and, as a large excess of these substances exercises a decidedly injurious effect both in mash tun and copper, it is advisable to get rid of this excess by adding sufficient quantity of calcium chloride or magnesium chloride to the water, whereby a portion of the alkaline sulphates is converted into alkaline chlorides, the calcium or magnesium chlorides being at the same time changed into sulphates. We thus get a water highly saline in character and possessing all the properties of a typical Burton water suitable in every way for pale ale brewing.

Having once ascertained the exact quantity of gypsum required to be added to the water either for the purpose of increasing the permanent hardness or for the destruction of the alkaline carbonates, it is very easy for the brewer to keep a check upon his gypsuming process as follows. In the case of non-alkaline natural waters, the total hardness of the water is determined, and the same after the water has been hardened. The first subtracted from the latter gives the hardness expressed as degrees of calcium carbonate (1° being equal to 1 grain of calcium carbonate per gallon) due to the gypsum dissolved up; this multiplied by the factor 1.36 will give the grains per gallon of calcium sul-

phate taken up during the process of gypsuming. This method answers admirably for all practical purposes, the error as compared with direct analysis not varying more than about  $\frac{1}{2}$  grain per gallon. For example:

*Non-alkaline water (v. Analysis No. 4).*

Total hardness before gypsuming . .	12.6
" " after " . . .	27.44
27.44 - 12.6 = 14.84 which mul-	
tiplied by 1.36 =	20.99
CaSO <sub>4</sub> found by direct analysis	21.23

Diff. .21 of a grain

In the case of alkaline waters the total hardness of the natural water is determined as before; then having found by trial the quantity of CaSO<sub>4</sub> necessary for the destruction of the alkaline carbonates and for the permanent hardness, the water is run through the gypsum tank at such a speed as to take up this quantity of CaSO<sub>4</sub>. As soon as the requisite amount has run through the total hardness of the treated water is determined. The amount of calcium sulphate in the water is next ascertained by chemical analysis, and the figures thus obtained taken as standards of comparison for all subsequent determinations. Thus an alkaline water containing 16.19 grains per gallon of alkaline carbonates, after hardening was found to have taken up 55.42 grains per gallon of calcium sulphate. Of this 17.92 grains were required to convert the alkaline carbonates into sulphates, leaving 37.5 grains of available CaSO<sub>4</sub>.

The total hardness of this water was 43.75. Hence 43.75° of hardness correspond to 37.5 grains CaSO<sub>4</sub>. Another determination of total hardness of this water after gypsuming was made some weeks later; this was found to be 45.5. Therefore

$$\frac{45.5 \times 37.5}{43.75} = 39 \text{ grains of available CaSO}_4.$$

This does not give such accurate results as in the case of neutral waters, but is quite near enough for all practical purposes.



8. Having glanced briefly at the composition of various types of water and the advantages or disadvantages they possess from the point of view of the brewer, we now proceed to consider the relative effects produced on the malt wort by the several mineral constituents usually found to occur in water.

As has been seen from the tables of analysis on page 352, the quantity and character of the various mineral substances found in natural waters vary considerably, and depend on the nature of the rocks through which the water percolates. An interesting series of analyses of water from the different geological formations of England has been made by Dr. E. Frankland, and published by him in his work on Water Analysis, and to which the reader is referred.

The most frequently occurring substance in solution in natural waters is calcium carbonate associated to a greater or less extent with magnesium carbonate. These carbonates are held in solution by the carbonic acid which is always present in natural waters; they probably exist in solution as bicarbonates. On boiling, this excess of carbonic acid is driven off, and the calcium and magnesium carbonates are precipitated. There is no doubt that these carbonates play a very important part in the brewing economy. Although a large portion of these salts is thrown out of solution during the heating of the water preparatory to mashing, yet the greater part of the precipitated carbonates remaining in suspension finds its way into the mash tun, and there combines with certain organic acids, principally lactic acid, always present in malt, forming soluble salts. This neutralisation of at least a portion of these organic acids must exert an important influence on the various processes which take place subsequently.

The amount of calcium and magnesium carbonates varies considerably, but 12 to 15 grains per gallon may be taken as a fair average. It is usual in those breweries where the waters contain very little or none of these salts to sprinkle calcium carbonate or chalk through the grist as it goes into the mash tun at the rate of 4 ounces per quarter of malt (about 10 grains per gallon of water).

Calcium sulphate occurs less frequently than the carbonate, but, with the exception of sodium chloride, exercises a more important influence on the mashing and boiling processes than any of the other salts present in natural waters.

A very interesting article on this subject by Southby appeared in the *Country Brewer's Gazette* for 1879, in which he proves very conclusively that, contrary to the opinion prevalent among brewers, calcium and magnesium sulphates, even when present in the brewing water in very large proportions, have no appreciable effect on the solubility of the nitrogenous matters of malt; their principal effect in the earliest stage of brewing operations is to greatly facilitate the ultimate fining of the beer by causing those matters which are rendered insoluble by boiling to separate in a flocculent form instead of in that minute state of division which results in the beer remaining obstinately cloudy, as so many brewers find to their cost. In addition to this, calcium sulphate possesses a decided antiseptic action, as worts brewed with a sulphated

water resist the action of the fermentative germs when exposed to the atmosphere better than those brewed with a softer water. The presence of calcium sulphates in a wort also prevents the solution of the coarser bitter principles of the hop, hence a brewer employing a sulphated water can use a much larger proportion of hops, if necessary, without rendering his ales excessively bitter. The same applies to magnesium sulphate. Valuable as the above sulphates are in the production of pale and mild ales, they are absolutely injurious in the brewing of porter and stout if present to the extent of more than three grains per gallon.

These results have been confirmed by Moritz and Hartley (B. J. 1883, 92); they find, however, that these sulphates extract more nitrogenous matter from malt than any other of the mineral constituents of water do, and Matthews (B. T. R. 1887, 295) is of opinion that these nitrogenous substances are of the nature of coagulable albuminoids. We must at the same time not forget that, by using a water containing appreciable quantities of calcium sulphate in solution, a large proportion, if not all, of the phosphoric acid existing in the malt, probably as potassium phosphate, is by double decomposition converted into acid calcium phosphate. It is well known that this substance exercises a powerful influence on certain albuminoid substances, especially at high temperatures. Hence the precipitation in flocks of these bodies, when the wort is boiled in the copper, is no doubt due in great measure to the action of this salt.

Water containing alkaline carbonates must undoubtedly be condemned as unsuitable for brewing mild or pale ales. It is well known that certain nitrogenous matters, whose presence in malt wort would have a most injurious effect, are freely soluble in slightly alkaline waters; these remain unchanged during the process of fermentation, and render the finished beer persistently cloudy, besides forming a suitable nidus for the development of various forms of bacteria. A large amount of colouring matter is also extracted from the malt by alkaline waters, whilst the diastatic action is considerably impeded; in the copper also certain resinous matters are extracted from the hops, which impart a bitter and rank flavour to the finished beer.

Alkaline sulphates if present in excess (more than 10 grains per gallon) have the same action, though in a very much diminished degree, as alkaline carbonates, more especially sodium sulphate. Potassium sulphate, on the other hand, if present to the extent of not more than 6 to 10 grains per gallon, has a decidedly beneficial effect, acting much in the same manner as magnesium sulphate.

Calcium chloride gives to the beer a harsh, coarse flavour.

Magnesium chloride, if present in small quantity, 2 to 4 grains per gallon, is supposed to be beneficial to fermentation.

With regard to the beneficial influence of sodium chloride in a brewing water there can be no question whatsoever. Some of the finest ales in the United Kingdom are brewed in districts where sodium chloride occurs in the natural well

waters to a larger extent than is allowed by excise regulations to be present in the finished beer.

Alkaline chlorides add considerably to the palateness of the finished beer, exercise considerable antiseptic properties during fermentation, and contribute to a general mellowness and roundness of flavour which without them is absent in the best brewed ales, mild or pale.

The question of nitrates is still a mixed one; the balance of evidence seems to be that where they are not derived from recent sewage contamination their presence in small quantities acts as a stimulus to fermentation, but a water containing more than 4 grains per gallon of potassium nitrate ought to be looked upon with grave suspicion, if not altogether condemned for brewing purposes, more especially as it is impossible to get rid of nitrates once they are found to be present in water. Nevertheless the fact remains that in several breweries where nitrated waters are used for brewing, the yeast keeps clean and vigorous and the ales are all that can be desired; but it is only fair to state that in such breweries sugar to the extent of at least one-fifth the quantity of malt is also used.

Iron in any shape or form is most injurious, but as it exists mostly in natural waters in the form of carbonate, it can be converted by oxidation into the insoluble peroxide and removed by subsidence or filtration.

The organic matter in water may be of two kinds, vegetable and animal; the vegetable organic matter is mostly of peaty origin, and as such cannot form suitable pabulum for bacteria, and first-class mild and light ales have been brewed from peaty waters after treatment with gypsum and kaimite; but on the other hand, where the organic matter is of animal origin, derived from sewage contamination containing such matter in solution, as it necessarily must be, the water, on biological examination will in all probability be found to be highly contaminated with disease germs; and although all of these germs as well as their spores are most unquestionably killed during the boiling of the wort in the copper, still such a water must be regarded as a dangerous one to use for brewing purposes as indicating the presence of matter in solution which neither boiling nor filtration can destroy or modify, and which at the first moment that favourable circumstances present themselves will serve to nourish and promote the growth of such germs of disease as may find their way subsequently into the beer or wort brewed from such a water.

**9. Barley.** The grain which for centuries has been most generally acknowledged to be best adapted for brewing purposes is barley. Of this cereal as many as 100 varieties have been cultivated in this country at one time or another, but the one most generally preferred by brewers is that known as the Chevalier.

The various species of cultivated barley are distinguished as two-rowed, four-rowed, and six-rowed according to the number of fertile spikelets on the ear. The first and last of these species are the most characteristic, the first including the finest varieties of English barley.

Originally in the United Kingdom malt for brewing was made from homegrown barley only; of late years, however, very considerable quanti-

ties are imported from other countries as France, Germany, Denmark, California, Russia, Egypt, Algeria, Chili, and New Zealand.

Some of these barleys are much superior to the English in appearance, whilst others, although presenting anything but a favourable appearance, are nevertheless not to be despised, fulfilling as they do a useful purpose when judiciously mixed with our own. This we shall see later on.

The quality of barley, as one would naturally suppose, depends to a large extent on the nature of the soil, climate, manure, &c.

Cold clay land, which is stiff or tenacious, no matter how well drained it may be, can rarely grow really good malting barley (Stopes on Malt and Malting).

Barley requires a warm, friable soil such as the calcareous loams &c. of Norfolk and the districts having a chalk subsoil, which are the best natural soils. Rich, loamy, or well-manured sandy, and other dry soils are also capable of producing fine barleys when the season favours them, especially if lime be present in fair quantities.

Barley flourishes best in the farmer's interest upon land well tilled and heavily manured, for it grows strongly and produces heavily. Such barley, however, is not the best for the brewer, for it has a higher percentage of certain nitrogenous matters which are decidedly injurious to the keeping properties of the finished beer. Hence the direct manuring of the soil for barley with nitrogenous manures (stable manure, salts of ammonia, and nitrates) must be avoided, such manures also produce a rank growth of the stalk and of the leaves; the barley is easily beaten down, and produces from this cause weak grains poor in starch.

Accordingly, Professor Farmer recommends that barley should follow wheat which in its turn followed roots. This seems to be reasonable enough, for it is now acknowledged that manures of a highly nitrogenous nature are decidedly prejudicial to the production of good malting barley. For malting purposes, the fine, full, well-developed bright grain is always the best.

Climate exercises a more important influence on barley than even soil or manure. Unfavourable summers and bad harvests frequently occur in this country. Indirectly, a bad summer, and especially a bad harvest time, will almost invariably cause such defects in barley that the production of really good malt is impossible. The difference in price may not be very great, if viewed from the standpoint of first cost, but the deficiency of extract and the inferior quality of the wort produced add largely to the actual loss of the brewer.

For the production of sound light beers quick in brightening, it is imperative to secure a barley of high vegetative capacity. With our varying climate and high farming, English barleys are less suited for this purpose than those imported from other countries, and the superiority of foreign barleys over English is, no doubt, to be attributed to the more suitable condition of climate under which they have been grown and harvested.

**10. Characteristics of barley.** For malting purposes Stopes groups the qualities of barley as under *four essentials*: vitality, condition,

maturity, odour, and six desirable non-essentials: size, weight, uniformity, colour, appearance of skin, age.

Upon the vitality of barley depends the growth, hence it is most important that the barley should contain as few as possible of non-germinating grains. The most trustworthy test for this is that of enforced growth, and for this purpose Coldeve's apparatus, fig. 2, is apparently the most effective.

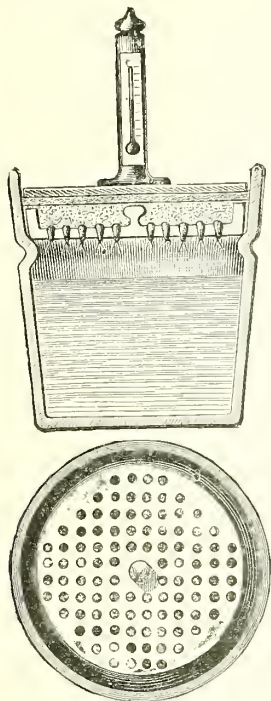


FIG. 2.

This consists briefly of a receptacle for water, a germination tray, and a felt cover fitted with a thermometer as shown in sketch. The corns to be tested are placed on the germinating tray, and receive the necessary moisture for germination with perfect equality from the receptacle underneath, whence the water evaporates without causing them to be exposed to an excess of moisture. The consequence is that corns of even quality not only grow as fast as they possibly can, but also perfectly alike, thus showing precisely the even or uneven germinating capacity of the grain, and as the tray is constructed to hold exactly 100 corns, the percentage is at once seen.

This test should show at the utmost only 4 p.c. of non-germinating grains. The above qualities may be briefly summed up:

The corns should not contain more than 4 p.c. of non-germinating grains.

When cut through, the cut surface should be white, friable, and mealy-looking; if it is fatty, glassy, or spotted, it is not to be recommended for use.

Barley ought to smell fresh and clean, not musty or mouldy.

The corns should be as nearly as possible of one size, plump and heavy, and free from other seeds. A good heavy barley should weigh from 50 lbs. to 56 lbs. per bushel; all under 50 lbs. may be deemed light. The grains should have an even light-yellow colour, with a thin wrinkled skin.<sup>1</sup> The actual judging of particular samples with regard to quality and comparative value is a matter requiring great practical experience and skill, especially as often the bulk is bought from a mere cursory examination of the sample in market. One of the great difficulties of the present day in addition to those resulting from bad harvesting and maturing of the grain is the prevalence of damaged and broken corn. It is more difficult than ever to procure samples that are perfect in this respect, owing to the carelessness so prevalent during the threshing of the barley by modern methods, for we may have not only broken corns which are easily detected, but other corns, apparently sound and good, that show on closer inspection slight abrasions of the skin occasioned during threshing by the too close setting of the machinery. This is a source of much trouble to the maltster, giving rise to mould on floors as well as to a large proportion of non-germinating corns.

11. Structure of barley. When a grain of barley is examined with the naked eye, a deep but narrow furrow may be observed running down the whole length of one side; the general appearance of this side is very convex, both laterally and longitudinally, hence it is known as the *ventral* side, and is the side which faces inwards when the grain is still attached to the ear. The outer or *dorsal* side of the grain is much flatter than the ventral. If next we cut through a grain of barley lengthwise with the furrow, so as to split it in two, three principal parts can be distinguished in it (v. fig. 3):

1. The hull or skin. 2. The endosperm or starch substance. 3. The embryo or germ.

The hull (x) or outer coat of the grain consists of the *paleæ* or valves formed of three rows of differently formed cells. The hull can be easily peeled off the barley grain after steeping, and under this is a shell tightly inclosing the grain; this is the pericarp of the fruit, and beneath this and closely grown together with it lies the

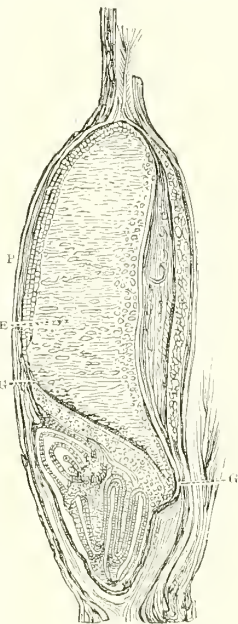


FIG. 3.

<sup>1</sup> Faulty grains are frequently sulphured, but can be easily detected by an experienced person on account of their unusually bright colour.



integument of the seed. The starch substance, or endosperm ( $\kappa$ ), forms by far the larger bulk of the barley grain, and consists principally of starch cells, surrounded by a continuous layer of smaller cells containing the various nitrogenous substances and fat.

The embryo, or germ, lies on the lower end of the grain, and its point or apex inclines towards the smooth or unfurrowed side. The lobe of the seed proper in the shape of a flat shield  $\sigma\sigma$  forms the boundary between the endosperm and the embryo; between this and the inner surface of the testa lies the germ, consisting of plumule or acrospire (future leaves and stalk) and the radicle or rootlets.

12. **Chemical composition of barley.** Those substances which go to compose the barley grain, as well as the other cereals used in brewing, may be classified as follows:

I. Carbohydrates. II. Resins and fats. III. Nitrogenous substances. IV. Ash.

The proportions of these several constituents vary with different kinds of barley according to circumstances of growth, manuring, harvesting, climate, &c.

1. **The carbohydrates** contain the three elements, carbon, oxygen, hydrogen, and are so called because they may be supposed to be derived from the union of a certain number of molecules of water with an equivalent number of atoms of carbon.

The principal members of this group are (a) *cellulose, starch, dextrin*; (b) *maltose, cane sugar or sucrose, raffinose*; (c) *dextrose, levulose*.

As the chemistry of the carbohydrates is fully treated of elsewhere, there is no occasion to refer further to this subject here.

II. **Fats.** Only small quantities of fat are found in grain, and very little is as yet known of the nature of the fat which occurs in barley. It may be obtained by treating barley flour with ether, which on evaporation leaves the fat as a thin yellow-coloured fluid of an agreeable odour.

**Resins.** The outer coatings of most cereals develop in ripening a certain amount of resinous matter, which by its comparative insolubility, protects the interior from premature access of water.

In addition to fat and resin a number of other substances free from nitrogen and which are generally classed with the resins are also represented in the grain of barley. Very little is known of them, but although present in minute quantity they nevertheless play an important part in contributing to the flavour and general appearance of each individual grain of corn.

III. **The nitrogenous substances** found in grain are much more complex in chemical composition than the carbohydrates; they all contain carbon, oxygen, hydrogen, nitrogen, and some of them sulphur as well. The nitrogenous substances known to occur in barley are *mucédine, fibrin, casein, and albumen*: of these fibrin is practically insoluble in water, mucédine is only slightly so, both are, however, soluble in alcohol, dilute alkali, and hydrochloric acid. Casein is slightly soluble in water, readily soluble in dilute alkali, but almost insoluble in dilute acid. All other nitrogenous substances occurring in barley are soluble in cold water and are included under the general term albumen.

The term albuminoid is applied to all the nitrogenous bodies present in barley, as it is extremely probable that the albumen is derived from some one of the other three, *i.e.* mucédine, fibrin, or casein. But little is known up to the present of the properties and changes which these bodies respectively undergo during the formation and subsequent germination of the grain.

Barley contains a certain proportion of nitrogenous substances termed albuminoids, some of which are soluble in cold water, whilst others are not. Of those which are soluble in cold water some are coagulated by heat at temperatures varying from about 40°C. up to 100°C. Among these soluble coagulable albuminoids occurs a body termed diastase, so named by Payen and Persoz in 1833 from *diastasis* (separation) (A. Ch. 53, 73), on account of its supposed property of separating the interior of the starch granules from their outer envelope. Under the action of diastase, starch which has first been gelatinised by boiling water undergoes a series of hydrations and successive decompositions resulting in the production of maltose and dextrin. This action, which is capable of taking place at 0°C., attains its maximum between 60° to 65° and ceases altogether at 80°. It seems very probable that diastase exercises a very marked influence on the insoluble albuminoids during the process of germination, converting them into soluble forms, and that during the process of mashing it acts still further on these soluble albumens, converting them into those other nitrogenous substances which are not coagulated by heat.

It has long been known that cold water extract of barley possesses distinct diastatic powers, but the diastase of barley has little or no action on starch paste. If, however, this starch paste be first treated with cold water malt extract at a temperature of about 75°C. for a few minutes, so as to bring it into the form of soluble starch or *erythro-dextrin*, then cooled to a temperature of 50°C. and some cold water barley extract added, the conversion of the soluble starch or higher dextrins into reducible sugars proceeds with great facility. Hence it must be assumed that the diastase of barley readily enough saccharifies starch when in a state of solution (as soluble starch) but has little or no effect on gelatinised starch or starch paste (Bungener and Fries, Z. f. d. ges. Brauwesen, 1866, 13).

If, however, an aqueous extract of barley be submitted for a few hours at a temperature of 30°C. to the action of ordinary yeast, its power of saccharifying starch paste is very considerably increased (Brown and Heron, J. C. S. 1879, 596), and there can be no doubt that the change which is induced here in the soluble albuminoids of barley by the living protoplasm of the yeast cell is identical with the action which goes on in the malting floors during germination.

It would appear then that malt contains at least two diastatic substances, one of which, formed during the *growth* of the barley, has not the power of transforming or saccharifying starch paste until it has been first converted into soluble starch; the other, formed during *germination* on the malting floors, possesses the power to a very marked degree of saccharifying starch

paste even at as high a temperature as 80°C.; but it seems extremely probable that these bodies are not simple chemical compounds of constant definite composition, but must be considered as a mixture of several bodies differing from each other in chemical and physical properties. For Brown and Heron (C. J. 1879, 596) have ascertained that when cold water extracts of barley and malt are heated up to different temperatures, for each increase of temperature there is a distinct and definite amount of coagulation of soluble albuminous substance, and at the same time a diminution in the diastatic energy of the solution, from which they conclude 'that the diastatic power of malt is a function of the coagulable albuminoids themselves, and is not due to the presence of a distinctive transforming agent.' There can be no doubt that during the kilndrying of malt a similar reaction takes place (Kjeldahl, Meddelelser fra Carlsberg Laboratoriet 1879) especially in the earlier stages of drying; a small proportion of the more easily coagulable albuminoids being rendered insoluble, the diastatic power which had attained its maximum at the withering stage, at the same time being diminished to a considerable extent. Indeed, it is a well-established fact, that a high dried malt will produce in the brewing a more highly dextrinous beer than one which has not been dried at so high a temperature on kiln.

The main object of malting is to induce certain changes in the nitrogenous constituents of barley, so that the soluble albuminoids or diastase already present may be rendered capable of transforming the starch, under the necessary conditions of heat and aqueous solution into those saccharine substances which are essential to the production of beer. The changes which take place during the malting process have been investigated by several chemists, but more recently by Behrend (Wochenschrift für Bierbrauerei, Dec. 1884), who finds that from the time the barley is taken out of steep the proportion of nitrogen per 100 corns continues quite constant during the whole process of germination, but the non-nitrogenous matter (starch) is eliminated to the extent of 10 p.c. He also states that from the first moment of germination the insoluble nitrogenous substances begin to undergo certain modifications by which they become soluble, and as fast as this soluble albumen is formed a certain proportion of it becomes further transformed into non-albuminous substances pertaining chiefly to the nature of amide compounds.

It is not certain whether the two processes are equally energetic, but it may be assumed on *à priori* grounds that at each instant of germination the solution of albumen and the formation of amides progress apace. If more albumen is brought into a condition of solubility than is decomposed into the crystalline products we have an accumulation, and in the opposite event a diminution, of the albumen. The practical application of this lies in the fact that Lintner (D. P. J. 251, 225) has come to the conclusion that under normal conditions the amount of diastase present in any given malt is directly proportional to the amount of soluble albumen contained therein. Hence if we determine the amount of nitrogen due to the soluble albumen and

assume that this soluble albuminous nitrogen is a measure of the diastase, by multiplying this by 6·25 we obtain the quantity of diastase, and on this assumption it has been found that the quantity of diastase in malt amounts to about 2 p.c. of dry substance.

The following table, deduced by R. Warington (Watts' Dict. viii. p. 143) from a compilation of all accessible analyses, numbering fifty-six in all, may be taken as showing a fair average composition of barley grain:—

1. Carbohydrates	. . .	63·66
2. Fibre	. . .	7·09
3. Fat	. . .	2·05
4. Albuminoids	. . .	10·58
5. Ash	. . .	2·57
6. Water	. . .	14·05
Total	. . .	100

Barley grain contains on an average less nitrogen than either wheat or oats; the proportion is least in fine malting barley, amounting to only 8 or 9 p.c. of albuminoids.

IV. The ash of barley grain, as calculated from 50 analyses by E. Wolf (Watts' Dict. viii. p. 143), has the following average composition:

Potash	. . .	K <sub>2</sub> O	21·35
Soda	. . .	Na <sub>2</sub> O	2·25
Lime	. . .	CaO	2·74
Magnesia	. . .	MgO	8·66
Ferric oxide	. . .	Fe <sub>2</sub> O <sub>3</sub>	·91
			35·91
Phosphoric anhydride	P <sub>2</sub> O <sub>5</sub>		35·19
Sulphuric anhydride	SO <sub>3</sub>		1·72
Silica	. . .	SiO <sub>2</sub>	26·10
Chlorine	. . .	Cl	0·88
			63·89

It has already been stated that land which has been highly manured with mineral salts containing a high percentage of nitrogen, such for instance as sodium nitrate or ammonium sulphate, will produce a heavy crop of barley. This of course from a farmer's point of view is decidedly an advantage, but such barley is always found to be exceedingly rich in albuminoids and consequently low in the percentage of starch. Hence for brewing purposes it is extremely unadvisable to use such a barley, for not only will the wort resulting from the malt made from this barley be poor in saccharine matter, but these nitrogenous substances, when present in too large proportions in the wort, exercise a very injurious influence on it, and cause the finished beer to become thick and cloudy and prevent its keeping sound for any length of time (L. Marx, Rev. Univ. de la Brasserie).

Therefore from a brewing point of view a barley rich in albuminoids must be regarded as of poor quality, while a low content of albuminoids in general is an expression of high quality. Hence Maereker (B. C. 1885, 696) concludes that the weight per bushel which is generally regarded as a fair criterion of the value of a barley can hardly be looked upon *alone* as a safe guide with regard to quality, but that the chief characteristics of a first quality barley are, 1, its consistency; 2, its colour; 3, percentage of

moisture; and 4, its percentage of albuminoids; these in first-class barleys should not exceed 8.6 p.c. He also finds that a grain possessing a fine, thin husk is found to yield the largest amount of starch; the kernels in this case should be thin and rounded, the percentage of husk being a minimum. This is the view adopted by Prof. Brewer, of the Brewer's Experimental Station, New York, as well as by C. Lintner (D. P. J. 247, 350) who gives 10.5 p.c. of albuminoids as a limit for first-class barley.

13. Preparation of barley for malting. Very little barley is in a fit condition for undergoing the process of malting when it is delivered at the brewery or malthouse by the farmer, as it generally contains several varieties of foreign seeds, fragments of pebbles &c. mixed up with it, as well as light and damaged corn. The following preparatory stages are considered by Stopes to be generally needed:—

Cleaning, grading, kilndrying or sweating. The dust which is generally found adhering to barley consists to a large extent of spores of numerous ferments and fungoid organisms, many of which find their way into the fermenting round, seeds of weeds and other foreign grains may also be present.

C. G. Matthews (J. R. Microsc. S. 1883) found that various kinds of barley, English as well as Saale, French, Chilian, and Californian, yield, when steeped for a short time in water, an abundance of mould spores, bacteria, and infusoria of various species, and from many experiments made by him he concludes that in the first stage of malting when the barley is put in steep the spores of various moulds and other micro-organisms are present in quantity in the steep water, being introduced into the cistern with the barley, and although the greater portion may be removed on withdrawal of the steep water, yet there would in all probability be left sufficient to cause a mould growth on injured or weakly corns whilst on the malting floor. Now it is a well-known fact that good, healthy growing, perfect corns are never found to develop growths of any kind of mould, the corns which appear to be favourable to such are always those which from various causes are incapable of carrying on a strong and healthy growth, having been injured by heating in stack, or sprouting, or, as is more generally the case nowadays, been split, crushed, or otherwise damaged during threshing, a slight abrasion of the skin in some instances being sufficient to give rise to development of mould. Hence it will be seen how very important it is that the barley should be cleaned and freed as much as possible from dust, broken corns, and all other matters which may in any way encourage the growth of mould on the malting floors, so that if a maltster wishes for clean floors he must first thoroughly clean his barley of such objectionable bodies by proper and careful screening. A form of screen which seems well adapted for this purpose is shown in fig. 4.

Grading grain is if possible still more important than cleaning it, as it is most desirable that for malting purposes all the corns should as far as possible be of one uniform size. The next process, and one of extreme importance, is the kilndrying of barley, or sweating as it is technically termed. With cold and damp seasons,

and with the modern fashion of threshing by steam either when carting or almost immediately after stacking, so that the grain has had no chance of sweating in stack, it is highly desirable that this should be done on the kiln, but like every other operation in malting it requires

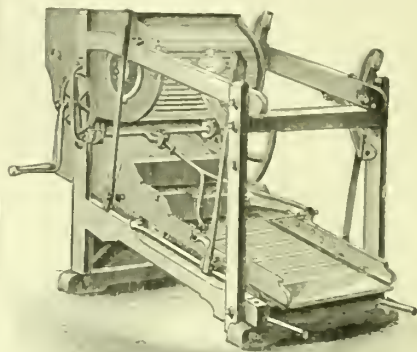


FIG. 4.—SELF-ACTING MALT-SCREEN.

discrimination and the exercise of judgment. Broadly speaking, almost every sample that has not been influenced by damp sufficiently to start the acrospire is decidedly the better for a few hours upon the kiln prior to storing or steeping. If the acrospire has moved, then drying does more harm than good.

Sweating is best carried on at a low uniform temperature, rarely exceeding 105°F. When dried it is advisable to store the barley in bins for at least a fortnight prior to steeping, in order that it may have time to mellow. The grain is now in a suitable condition for undergoing the various processes of malting; these are steeping, couching, flooring, withering, drying.

14. The great distinctive difference between malt and corn is growth; no matter what processes they may have been subjected to, any grains of the corn which have not grown remain as barley, wheat, &c., and are not malt. When a seed is placed under suitable conditions with regard to heat, light, air, and moisture, it begins to germinate or grow. When it begins to grow the first sign of a change taking place is the protrusion in a downward direction of the rootlets or radicle through the integument; at the same time the plumule or acrospire begins to start growing in an upward direction until it bursts through the integument and gives rise to the first leafy organs of the growing plant. When wheat commences to germinate, the plumule of the embryo on bursting through its envelope finds itself in immediate contact with the inner surface of the pericarp, which in this case not being sufficiently strong is ruptured, the plumule continuing its growth outside the grain.

In barley the pericarp is of sufficient strength (even in the so-called naked barley where the palea, as in wheat, is not adherent) to retain the plumule within it. In consequence of this the growth of the plumule takes place between the testa and pericarp, and in very close proximity



to the reserve materials of the endosperm, until it finally issues at the end of the grain the farthest removed from the embryo.

15. The water used for wetting or steeping should be of such purity that it may pass as drinking water. Waters containing much organic matter, especially that derived from animal sewage, frequently contain salts of phosphorus, which coming in contact with the numerous spores of bacteria and mould on the surface of the barley afford a most favourable medium for their development and growth. Certainly the water in which barley has been steeped affords itself very suitable nourishment for these micro-organisms, and where the water helps in the same direction the result is self-evident.

Of the mineral matter in water iron in any form is most objectionable, as it gives rise to the insoluble phosphate of iron.

Chlorides of the alkalis if present in large quantity remove a considerable proportion of mineral as well as organic matter, whilst they retard germination to a considerable degree (Michel and Handwerek, B. C. 1882, 486).

The presence of calcium chloride hinders the extractive action of sodium chloride to a certain extent (*ibid.*).

Calcium and magnesium carbonates and sulphates are generally supposed to fix the phosphoric acid in the grain, the potash and magnesia being extracted by the hard water whilst the lime enters into combination with the phosphoric acid, forming an insoluble phosphate in the grain (Ullick, B. C. 1882, 40-42), but Mills and Pettigrew find that the more of these mineral salts there are in steep water the more mineral matter there is extracted from the barley (J. C. S. 1882, 38). They are confirmed in their results by Michel and Handwerek (D. P. J. 247, 82, 163, and 214). From a series of experiments made by the author on the steeping of barley, where—1, distilled water alone; 2, a water containing 13.8 grains of calcium carbonate per gallon (*v. Analysis* No. 2, p. 352); and 3, the same with 30 grains of gypsum added, were employed, the following results were arrived at: that the total matter extracted by water No. 1 was in all cases the greatest, that by water No. 3 least; that this applied to the mineral as well as the organic matter, but whereas No. 1 dissolved out the most mineral matter, No. 3 extracted the most phosphoric acid.

As regards the extraction of organic matters all observers are pretty well agreed that a soft water extracts more than a hard one.

It will be readily seen from this that in no case should a water containing even only a small quantity of alkaline carbonates be used for steeping; the same remarks apply to alkaline sulphates.

Mills and Pettigrew conclude that nitrates have a highly stimulating action in the germination of malt, and recommend the addition of a small quantity of calcium nitrate (about 3 grains per gallon) to those waters which are deficient in nitrates.

The principal object of steeping is to moisten thoroughly every portion of the grain, so as to enable it perfectly to perform the functions of germination, and the water that will leave

within the grain as much as possible of its natural constituents, whether mineral or organic, is undoubtedly the best for steeping purposes—such a water will generally be found to be that supplied for drinking purposes to most towns.

16. **Malting.** At present three systems of making malt are practised:

1. English system.
2. Continental.
3. Pneumatic.

The English system<sup>1</sup> briefly consists in steeping the grain in water in large iron or stone cisterns, draining the water off, spreading the moistened grain in thin layers upon exposed floors and drying upon an open fire kiln at a period of from 9 to 21 days from time of steeping.

The continental system differs materially in all the above details.

Pneumatic malting provides for absolute control over the admission of air supplied to the germinating grain.

The simplest form of malt-house possessing any capacity for work is a plain two-story building having attached to it a kiln or drying-house, and consisting of a ground-floor of clunch, a brick steeping cistern, and a first floor of timber with or without partitions for separating the stored grain or malt: but a good malt-house of fair size is most conveniently and favourably worked if it consists of one main building of three stories—two kilns and a corn or malt store.

The growing floor may be composed of a variety of materials, but that which is most to be preferred is cement concrete worked to a perfectly smooth face.

The cisterns should always be at the end opposite to the kiln in a single-floor house, and so arranged that entire control of the temperature of the steep liquor can be secured, and that the grain can be readily screened into them when filled with water to enable the thin corn and refuse to float off.

The water must also have command of them so that it can be run in from below and overflow at top prior to a charge of steep liquor, and a number of inlet and outlet pipes, all fitted with strainers, should be fixed. They should possess in addition a series of perforated pipes, by means of which water can be sprayed or sparged from above over the grain like a shower. The cisterns are emptied of the steeped grain either by shovelling on to the floor, if on the same level, or by running down through shoots in the bottom to the floor below.

Cisterns are generally built of concrete or brick. An excellent form of construction is afforded by the use of the Hygeian Rock cement, as shown in fig. 5. This method gives a wall only 9 inches thick, but quite strong enough for all practical purposes; the outside wall of the cistern is generally coated with cement, whilst the interior of the cistern is preferably lined with white glazed or enamelled bricks well set in cement. Brick or concrete cisterns should have a wide central channel running their full

<sup>1</sup> For much valuable information on the subject of malting the author is indebted to a most comprehensive treatise on malt and malting by H. Stopes, from which several of the woodcuts illustrating this portion of the subject are taken.

length. The top of the channel must be framed to receive perforated iron plates or tiles to serve as strainers. The capacity of these eisterns should be ample enough to steep the utmost quantity of corn the floor can possibly grow in the coldest weather; not less than 14 cubic feet per quarter should be allowed when calculating their dimensions.

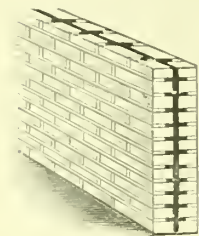


FIG. 5.

The kiln should be a lofty and roomy structure, preferably of brick, with a high roof surmounted by a cowl. The area of the drying floors should never exceed one-fourth or be less than one-sixth of the growing floors, nor should the combined air inlets and discharges bear a ratio to each other exceeding that of 4 to 5.

In practice it is found that the more closely a kiln resembles a chimney in construction, the greater is its effective capacity, consequently the tendency has been constantly to increase the height of the kilns. Kilns may be of various forms, but a square one is undoubtedly the best. In fig. 6 is shown a type of kiln very common in Great Britain.

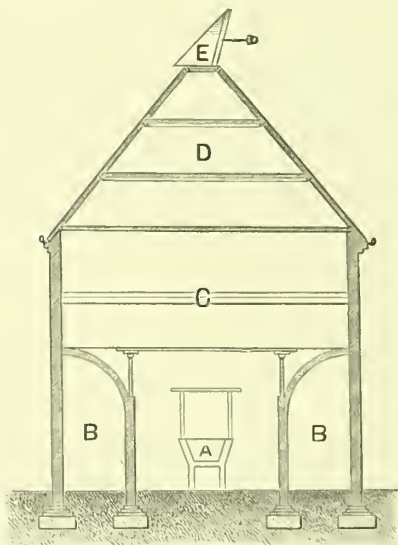


FIG. 6.

In every portion of the plant connected with malting, great diversities of size and style occur, and kiln furnaces offer no exception to the rule. Generally maltkiln furnaces either permit the products of combustion to pass through the malt whilst drying or they do not do so. The form of furnace perhaps most in vogue is known as the fire-basket. This is a large open east-iron basket of from 3 to 6 ft. square, with legs or supports carrying a frame fitted with ordinary fire-bars and thick sloping sides. These baskets are sometimes placed merely upon the bottom

floor of the kiln with no protection of any kind, others are built over with a brick arch left full of holes for the escape of heat on all sides. A in fig. 6 shows the form of fire-basket usually employed, the spaces *nn* at the sides of the

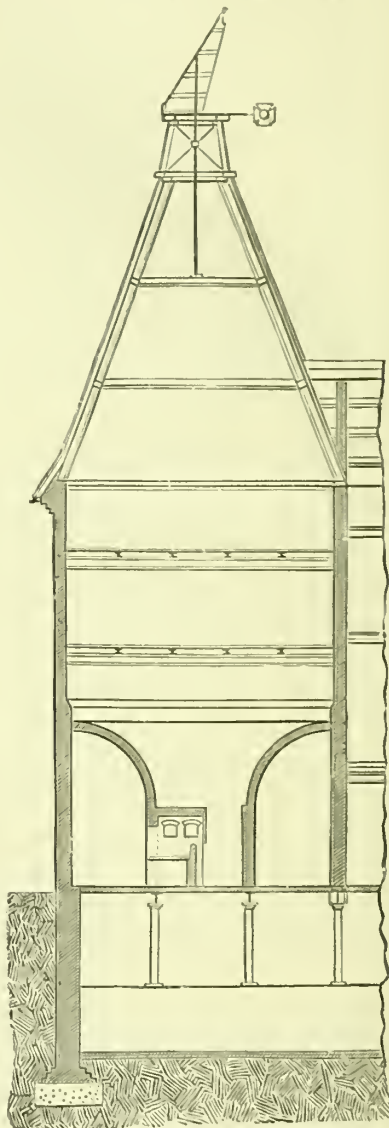


FIG. 7.

furnaces are used as coal or fuel stores. The drying floor *e* is built at all heights, ranging from 5 to 29 ft. above the furnace, and is generally made of earthenware perforated tiles resting on light iron bars, which in their turn are supported by larger joists. Of late years steel wire, of varying width and from 30 to 36 inches in length, has been introduced for kiln floors, and seems to possess decided advantages over the ordinary tiles.

The construction of the roof *D* is of great importance, as very much depends on it; if the pitch is not at the proper angle the drying of the malt is affected to a certain extent; cross timbers are objectionable and should be avoided as far as possible; lath and plaster forms the best lining to the slate roof as well as for the sides of the drying chamber.

The cowl *E* is the usual form of outlet to most English kilns. Until very recently all kilns were built with only one drying floor, but in 1881 the first kiln in England with two floors, and known as Stopes' system (fig. 7), was erected by Messrs. Taplin & Sons at Brighton, which gave very satisfactory results, and is now being introduced into many breweries in this country. It is claimed that two-floor kilns possess several advantages, of which, probably, the chief are the regularity of temperature upon both floors and the economy of fuel and labour.

**17. Steeping.** The cistern should be filled with the steep water, then the barley slowly run through a shoot into the cistern; by this means the dirt and dust, small and light corns, and other matters find their way readily to the surface and may be skimmed off. This first steep water should be run off within the first six hours, it being the most impure; the succeeding steep water should be changed every twelve to twenty-four hours, according to temperature and season of year.

The first steep water should be run off from above, and the second water run in from underneath; this upward filtration serves very effectually to cleanse the grain from any adhering impurities. The grain is allowed to remain in steep for a period of forty to seventy hours, depending upon surroundings; but the maltster would naturally be guided by the temperature of the atmosphere, the quality, condition, and age of the barley, high temperature necessitating more frequent changes of steep water and shorter time in steep. Then, again, coarse, thick-skinned, or heavy barleys would naturally require longer steeping than the lighter and thinner kinds; the older the barley the longer it requires to be steeped, as new barley germinates more quickly than old, the chief object of steeping being to impart to the grain about to be malted a sufficiency of moisture to ensure perfect and regular germination.

**18. Couching.** Before the repeal of the malt tax the barley when taken out of steep was placed in what was known as the couch. This might be regarded as a dry cistern where the grain had to lie a certain number of hours, or until it was gauged by the excise officer and the duty levied. Since this has been done away with the couch is no longer needed, though even yet many maltsters pile up the barley when taken out of steep in a heap for twenty to twenty-four hours, indeed until the growing point of the rootlet begins to show. This is a great mistake. In the first place a greater amount of heat will be developed in the interior of the heap than on the outside by the germinating grain, hence these corns will grow more rapidly than the others, so that very uneven 'pieces' on the floors will be the result. It has also been proved that heat in couch tends directly to produce acidity in the finished malt. After

the grain comes out of steep it requires all the oxygen it can get, as well as the removal of the carbonic acid gas which becomes disengaged by the process of germination; this necessarily involves free contact with air and therefore it is advisable that couching be done away with altogether.

**19. Flooring.** Where it is still practised, as soon as germination is observed to have commenced, the couch is broken down and the grain spread out on the floor, the depth at first varying from twelve inches to about three or four according to season and temperature; it is then left so for twenty to twenty-four hours, when it is turned by means of a wooden spade. For the succeeding two or three days it is either 'ploughed' or turned about twice daily; of course this entirely depends on the judgment and experience of the maltster, his main object being to obtain a good bushy root and a regular development of the acrospire. This requires very careful and close attention on the part of the maltster, for during 'flooring' he has not only to control the development or growth of the germinating grain, but the very nature of that growth. He has to give air and secure ventilation, to regulate heat and humidity, to foster the development of the acrospire and check the root growth, or *vice versa* as the case may be; all this can only be attained by long experience and an intelligent appreciation of scientific facts.

As a rule, English maltsters allow germination to proceed until the acrospire has extended to about three-fourths the length of the grain, the rootlets being at the same time about twice the length of the grain, but this is varied considerably according to the ideas of each individual maltster. Germination is accordingly carried on until this stage is reached.

About the fifth day from the time of taking out of steep the grain is sprinkled at intervals with water from a watering-can; this is continued until the sixth day. The quantity of water used for this purpose varies from three to six gallons per quarter of barley, but of course will naturally depend upon the state of the atmosphere as well as on the condition of the piece. On the days of sprinkling the grain is turned four times each day; after the sixth day it is turned two or three times daily. As soon as the germination has proceeded to such a degree as may be desirable, it is subjected to the process of withering, the object being to arrest germination, to increase the temperature of the piece so that as large an amount of moisture as possible may be got rid of preparatory to kilndrying. In many malt-houses a proper withering floor is provided, generally of wood. During this stage the rootlets wither, becoming shrivelled and dry. As soon as this takes place many maltsters throw the green malt, as it is now called, into a heap, and allow it to heat spontaneously, the object being to make it tender.

A piece which was sprinkled on the fifth and sixth days under ordinary conditions should be ready to go on kiln on the tenth or eleventh day.

Some maltsters allow the piece to become almost dry, not sprinkling until the eighth or



even ninth day, but this cannot be recommended. The grain at time of going to kiln is at most only imperfectly withered, contains an excess of moisture necessitating very frequent turning as well as encouraging the growth of mould on kiln, and finally imparting a degree of hardness or steeliness to the finished malt which occasions diminished extract and possibly starchy worts.

If the barley whilst on the floors shows much, or in fact any signs of mouldiness, both the eistern and floors must be thoroughly well scrubbed with water to which 10 p.e. of good strong calcium bisulphite has been added. When dealing with low class, ill-conditioned, or damaged grain it is always well to add a suitable quantity of bisulphite, both to the steep water as well as to the water used for sprinkling.

It is also essential that thermometers should be placed at frequent intervals on the floors, and the temperature carefully noted from time to time; indeed, the question of temperature is just as important a factor in malting as it is in mashing.

**20. Drying.** By the time the germinated barley is ready to go on the kiln, it really is in effect no longer barley but malt, or more properly green malt, and has attained at this stage its highest diastatic energy, so that if the object were merely the production of diastase the malt might now be dried off at ordinary temperatures; but for the purposes of the brewer and distiller it is absolutely necessary that this green malt be subjected to the influence of heat, not only for the purpose of drying it completely and arresting germination, but in order that certain changes may take place in the chemical composition of its various constituents which are necessary to impart that flavour and other properties to the liquor brewed from it and which we term beer. In addition to this the malt also becomes capable of lengthened storage, and when well dried is best adapted for grinding and for transport; also all mould and fungoid growths are completely arrested and their vitality suspended.

The temperature employed in finishing off the malt on the kiln will determine its quality, thus we may have pale malts, medium and high dried.

For pale malt only the better qualities of barley should be used, and great attention should be paid whilst on the growing floor to prevent the development of mould; also the withering off should be carefully attended to, the principal object of the maltster being to obtain a good healthy growth in the earlier stages, and that the green malt should be as dry as possible at the time of going to kiln.

To dry pale malt well, Stopes says three things are necessary:

1. It should be loaded in the condition just described as sound green malt upon a floor at a thickness rarely, if ever, exceeding 7 to 8 inches.

2. It must remain *unturned* at a low temperature until nearly all moisture is removed.

3. Heat must then be applied steadily and freely, and be maintained for a considerable time at a nearly uniform temperature, ranging from 100° to as high as 230° in some cases.

As long as an appreciable amount of moisture remains in the malt, it is most important that the temperature on kiln should not exceed 120°, while special attention must be paid to ventilation. When we consider that from 90° to 120° is the most favourable range of temperature for the development of the numerous spores of various micro-organisms which, despite all our efforts to the contrary, are to be found adhering to the moist corns, and that with their development ensue chemical changes, such as the production of various organic acids, which most seriously affect the character of the malt, it would seem that the shorter time the malt is exposed to this temperature the better; therefore it is advisable that the layer of malt should certainly not exceed eight inches, and it would be better still if it were only six. But it is not simply a question of drying the malt quickly at a low temperature; undoubtedly certain changes irrespective of those produced by micro-organisms are brought about in the nitrogenous as well as in the other constituents of the malt whilst submitted to these conditions of temperature and moisture, of which absolutely nothing is as yet known.

As soon as the malt begins to present a dry appearance, the temperature may be gradually raised up to the final temperature at which it is to be finished off. It is impossible to give a fixed limit for this, as a great deal will depend upon circumstances, but as a general rule, for pale malt the final temperature may be taken at 180° F. From the time of raising the temperature until the end of the process, the malt should be turned at intervals.

In drying the malt the great point to be observed is the maintenance of a perfectly even temperature, so that the whole of the malt drying should be at any given moment of the same uniform temperature. Now it is impossible to obtain such a result with a single-floor kiln, as great a difference as 75° having been observed between two given portions of malt on the same kiln floor, and this in a house supposed to be constructed on the best principles, but having a single-floor kiln. However, by frequent turning this defect can be obviated to a certain extent.

The process of drying, from time of going on to coming off kiln, usually occupies about 4 days, and is distributed as follows:

1st day	not below 80° or above 100°
2nd "	" 90° " 110°
3rd "	" 120° " 130°
4th "	" 140° " 180-185°

For the first two days the malt should on no account be turned, but the surface forked over lightly if needed. After the second day, on single-floor kilns, the malt should be turned at frequent intervals. Medium and high dried malts are finished off at much higher temperatures, ranging from 200° to 230° and upwards.

As soon as the temperature gets up to the final point this heat is in a great many maltings maintained only for one or two hours. This is a great mistake; there can be no doubt that the longer the malt is exposed to a high heat, the sounder and better keeping will be the resulting beer. The final heat might certainly be attained

in a shorter time than it usually is, and the malt might be exposed to this heat for at least 6 hours without undergoing any darkening in colour whatever.

Much the same method is pursued in the drying of the malt on double-floor kilns as on single. The malt is first loaded on to the top floor, where it is kept at a temperature not exceeding 120° until about 90 p.c. of the moisture is driven off. It is then dropped through doors or holes to the lower floor, where it is finally dried off at a temperature of from 180-190° or more, and the same heat and air that effect this are in fact the very best possible to drive off the moisture from the upper floor, which in the meantime will have been loaded with a fresh piece.

Recently a new form of kiln, known as Free's Patent Malt Kiln, has been devised, and which is said to give excellent results. This system consists in the rapid removal of the moisture from the malt when first put on kiln, by increasing the draught of warm air through the layer of malt, and depends on the one condition that the kiln should be practically an airtight chamber. At the apex of the kiln is a shaft into the shoulder of which is fitted a Blackman air-propeller. As soon as the green malt is loaded on the kiln this air-propeller is caused to revolve at a very rapid rate and the motion thus produced is so great that a partial vacuum is formed in the kiln and the moisture is accordingly drawn away quickly from the malt without any of the accompanying reek so prevalent in ordinary kilns. It is claimed that by this means the actual drying of the malt is accomplished in much less time than by the ordinary methods, at a higher temperature and more perfectly than heretofore.

It is hardly necessary to say that in the process of kilndrying, where the temperature is the important factor, several thermometers placed on each floor are absolutely indispensable.

The malt, after it is finished drying, has yet to be freed from the radicles or 'combes.' This is accomplished by its being well trodden by men furnished with heavy-soled boots; the radicles are thus detached from the corns, and by passing the malt over a 'water-fall' malt screen it is completely freed from these as well as from some of the adhering dust. In some maltings, previous to being trodden the malt is heaped up in the centre of the floor and remains so overnight with the fire well banked up.

We may get a very fair idea of the temperature at which the malt has been dried by observing the colour of the combes. The higher the temperature the more highly coloured they become; indeed, where it is almost impossible to observe any difference in the colour of two malts dried at different temperatures, an examination of the combes from these malts shows it at once.

**21. Storing.** After freeing from the combes by screening, malt is usually stored away in bins for some weeks previous to use in the brewery. The floor, sides, and top of these bins should be made of good seasoned wood and lined with sheet zinc. These bins are usually built in the driest part of the malt-house; this would naturally be in the neighbourhood of the kiln, and

it should be protected as much as possible from draughts.

During this storage of the malt previous to use some change certainly takes place in its nitrogenous constituents; in technical language, 'the fire is taken out of it and the malt becomes mellow,' but, whatever these changes are, nothing is known about them up to the present. All that can be said is that it has been found decidedly inadvisable to use any malt for brewing purposes until it has been stored for at least six weeks from time of coming off the kiln.

**22. Characteristics of malt.** The following are the characteristics of a good malt as given by Stopes:—

1. *Growth.* The malt should be evenly grown, the acrospire showing between two-thirds to three-fourths up the back; any malt which contains many corns showing the acrospire protruding should be rejected. On the other hand, it should also not contain more than 4 p.c. of ungerminated corns.

2. *Slackness or moisture.* This will vary to a slight extent with the age of the malt, but on the average, malt should not contain more than 3 p.c. of moisture.

3. *Age.* Malt is at its best from six weeks to four months; after that time, under ordinary conditions of storage, it gradually absorbs moisture and becomes more or less slack.

4. *Odour.* Good malt should have a pleasant well-known aroma peculiar to itself.

5. *Condition.* This will depend a good deal upon the quality of the barley. Good barley badly managed may produce a bad malt, but a bad barley will never produce a good malt. Good malt should be tender and friable when broken, and should bite crisp and crumble readily under the teeth.

6. *Cleanliness.* Malt should be comparatively free from mould and dust as well as root-lets and inorganic refuse.

7. *Flavour.* The flavour of malt is derived from influences of growth and of drying; it should possess a pleasant, mellow, sweetish taste, free from rawness on the one hand and bitterness on the other.

Such are the characteristics of a good malt so far as can be determined by the eye, but these should always be supplemented by a complete chemical analysis.<sup>1</sup> By this means we may obtain the following results for malt:—

I. Actual composition:

- a. Starch products, as dextrin and maltose.
- b. Cane sugar.
- c. Other sugars.
- d. Total albuminoids soluble after boiling.
- e. Ash.
- f. Moisture.
- g. Insoluble matters or grains.

II. Relative diastatic capacity.

III. Specific rotatory power.

There can be very little doubt that a brewer ought to have a fair idea of the constituents of his malt before commencing to mash with it, for from such an analysis as given above he will

<sup>1</sup> For full details of latest methods of analyses of malt, worts, and beer, see Heron, *The Polariscopes and its Applications to Brewing*, S. O. I. 1888; also *Transactions of Laboratory Club*, I, 97.

be in a position to predicate very fairly what kind of wort and beer his malt is going to produce, and so be enabled to control not only his mashing process but all subsequent operations.

Other descriptions of malt, in addition to the kind we have hitherto been considering, are made and used. These are:

Brown or porter malt.

Amber malt.

Black, roasted, chocolate, or patent malt.

Brown and amber malt are prepared practically in the same way as ordinary malt until they go on kiln. Here they are dried at a much higher temperature, and wood is largely used for the purpose instead of coal or coke.

Black malt is simply ordinary malt which is roasted in exactly the same way as coffee berries are. 'A sample of properly roasted malt is uniform in colour, of a chocolate hue, not black, and each corn clear and clean. If it is black, with the corns burst, and especially if matted or run together, it is of a most inferior kind, and neither good flavour nor permanent colouring can be expected from it.'

**23. Malt adjuncts.** These may be divided into two classes. First, those substances from which the extract has to be obtained by the mashing process, and second, those in which the extract is already formed.

**Class I.** Several grains of cereals other than barley have been prepared for brewing purposes, either by malting or subjecting to the action of heat in some way or other. The principal of these which are at present used as substitutes for malt either in a prepared form or in the raw state are maize malt, germless maize, gelatinised maize, gelatinised rice, torrefied grain or white malt, and in the raw state barley, rice, and maize. When using any of these substances for brewing purposes certain proportions of them are either mixed with the malt in the mash tun, or else the starch contained in them is first gelatinised in a separate vessel and rendered soluble by the addition of a little malt, and afterwards added to or sparged over the goods in the mash tun.

**Class II.** Under this head are included ordinary cane sugar, invert sugar, glucose or starch sugar, and dextrin-maltose.

Raw cane sugar cannot be recommended as a brewing material, owing to the large quantities of impurities of a dangerous character which are always present.

Refined cane sugar is used to a certain extent, but before it can undergo fermentation it has first to be hydrated or inverted by a peculiar unorganised ferment contained in the yeast and termed invertase, and as this reaction tends to weaken the yeast to a certain extent as well as favour the production of lactic acid, it has been found more advantageous to use cane sugar which has been previously inverted. This is done by means of sulphuric acid, which is afterwards neutralised with calcium carbonate, and the inverted sugar freed from the calcium sulphate by filtration is further purified by being passed over animal charcoal, and then boiled down under diminished pressure to a thick syrup, in which state it is sent out by the manufacturer.

**24. Hops.** The hop plant belongs to the nettle family, and is a perennial climbing or rather twining plant. It is found in the wild state all over Europe, and is propagated not by seed but by sets or suckers thrown up from the root, which is perennial, the stems dying down at the approach of winter, and fresh ones coming up each spring and often attaining a height of thirty feet or even more. The hop plant bears two distinct kinds of flowers, male and female, and these flowers again are produced on distinct plants; of these only the plant bearing female flowers is cultivated, the male plant being rigidly excluded from most hop plantations. The flowers, which are the only parts of the plant of any use to the brewer, occur in the form of peduncles or cones, consisting of a series of scales or carpels lying above each other so as to form a cone. On the inner side and on the lower edge the carpel is turned over and incloses at first the female flower and afterwards the fruit developed from the flower. The fruits of the hop are round hard granules or little nuts; these fruits and the inner sides of the scales are thickly covered with a fine yellow dust—the so-called lupulin. Under the microscope this dust is seen to consist of numberless granules, these granules being composed of glands, which are formed by the union of several simple cells. These glands are hollow, and this hollow space is filled with hop oil, resin, bitter principle, &c.

As a rule, the value of the hop may roughly be determined by the quantity of lupulin it contains.

Hops are principally cultivated in the counties of Kent, Surrey, Sussex, and Worcester. The Kent hops are in much repute, and more especially that variety known as Golding, being rich and delicate in flavour; the Sussex hops are somewhat coarser in flavour than Kent, and perhaps do not present such a pleasing appearance to the eye, but nevertheless are good useful hops for running beers or for mixing with Kents for higher-class ales.

Worcester hops are milder than the above, and in some breweries much preferred to any other. Of late years bad seasons and the attack of the hop-aphis have done much to deteriorate the quality of English hops, so that at present large quantities are imported from Germany and America; but foreign hops lack that delicate aroma and flavour peculiar to English growth, and are as a rule only used for the lower quality beers. Hops, in order to be kept for any appreciable time, require to be thoroughly dried; the hop cones, after they are picked, are spread out on the floor of a kiln, where they are dried by artificial heat. Sulphur is often sprinkled on the kiln fires, and the sulphurous acid gas thus produced passing through the hops bleaches them, so that hops naturally dark in colour or unsightly in appearance are rendered more pleasing to the eye and fetch a higher price. Thausing claims that it is decidedly beneficial to subject hops to the sulphuring process on kiln; but, unless where the mildew and other parasitic diseases have made their appearance, sulphuring is decidedly injurious as well as encourages fraud. On the other hand, it seems to be a pretty general custom nowadays to



sprinkle the hop plants whilst growing with flowers of sulphur, to prevent or destroy certain diseases which attack the plants at various stages of their growth—such as mildew and blight—but it is evident that very little of this is to be found on the hop cones after picking; but even if any should remain adherent, being present as free sulphur it can have little or no effect on the constituent principles of the hop.

In order to estimate the value of hops without having recourse to analysis, the following physical features may be taken into consideration: the fineness of the aroma, the proportion of lupuline which the cones contain, the proportion of stalk, seeds, and impurities which accompany the hops, and the general appearance of the cones themselves.

**25. Chemical composition of hops.** Hops contain, besides cellulose, woody fibre, water, and ash, certain substances, more or less soluble in boiling water, and which give that agreeable bitter and aromatic flavour to beer. These consist of hop oil, resins, bitter substance and tannin, but up to the present very little is known of any of these bodies.

The hop oil is an essential oil, giving to the hop its characteristic agreeable smell. It is present to the extent of about 0·8 p.c. in the glands of the hop cone, and may be obtained by distillation in a current of steam, the volatile oil floating upon the surface of the condensed water in the receiver, from which it may be separated by decantation. During the boiling of the hops with the wort in the copper the greater portion, if not all, of this oil becomes volatilised and lost to the brewer; hence a process has been recently introduced for extracting this oil from the hops previous to boiling, and afterwards adding it either to the wort before ordinary fermentation or to the finished beer.

When obtained from fresh hops, the oil has a light yellow colour, hot burning taste, and agreeable aromatic smell. It is only slightly soluble in water, but freely so in alcohol, ether, and light petroleum. Not only is the hop oil volatilised at temperature of boiling water, but also slowly at ordinary temperatures and by exposure to air is easily oxidised into volatile acids, especially valericianic acid, to the presence of which the peculiar odour found in old hops is due.

This hop oil is generally found intimately mixed up with resin, which it seems to be capable of dissolving to a certain extent. It seems very probable that the resins of the hop (three of which have been determined) are the results of the oxidation on the one hand of the hop oil, and on the other of an organic acid. Bungener (*Bl.* 45, 9), who has isolated it from hops and studied its properties, has termed it lupulinic acid. Hayduck (*Wochenschrift für Brauerei*, 1887, 347) has detected three different resins in hops—one a soft resin, precipitable by lead acetate and soluble in petroleum ether; a second also soft resin, soluble in petroleum ether, but not precipitable by lead acetate; and a third one hard and solid, not soluble in petroleum ether and not precipitable by lead acetate. Experiments made by Hayduck show that the second of these resins is identical with the soft resin formed by the oxidation of Bungener's lupulinic acid, whilst the third resin is due to the oxidation of hop oil. Hayduck

also shows that the soft resins possess highly antiseptic properties, whilst the hard one checks to a certain extent the rapidity of fermentation. It was found that when these resins were repeatedly extracted with water the aqueous solution gradually decreased in antiseptic power; hence it clearly tends to show the unadvisability of boiling hops more than once, since the first boiling would probably extract the greater portion of the soft and more soluble resin.

The tannic acid which occurs in hops is a fawn-coloured powder, easily soluble in water and weak alcohol but insoluble in ether. In aqueous solution it gives a dark-green colouration with ferric chloride, and possesses the property of precipitating in flocks the albuminous bodies of malt wort. It is therefore an eminently useful substance in the manufacture of beer. From the foregoing it will be readily seen that really the only substances in hops of any use to the brewer are the soft resins and tannic acid. These soft resins are readily oxidised into the hard and insoluble variety, while tannic acid is capable of being converted in like manner into gallic acid, a substance possessing very few of the properties of tannic acid. It is not then a matter of surprise to assert that old hops are of little or no value, for considering the loose manner in which they are housed in most breweries, subject to every variation of temperature and freely exposed to the air, changes in the composition of the active principles must of necessity take place in a more or less rapid time, rendering them eventually of little or no value to the brewer. Therefore, in order that hops may retain to a certain extent those active principles intact for an appreciable time, they should, after drying and pressing, be packed in airtight tin cases, which should not be opened until the hops contained therein are required for use.

**26. Yeast and fermentation.** Before the classical researches of Pasteur various theories were advanced to account for the phenomena connected with fermentation, but he was the first chemist who proved that the process of fermentation was due, not to a peculiar protoplasmic substance secreted by the yeast fungus, but that the presence of the plant itself in the saccharine liquid is essential to alcoholic fermentation, and that the yeast cells have the power, in the absence of the oxygen of the air, of splitting up sugar into alcohol and carbonic acid, and deriving the oxygen necessary for their support and nourishment by that means.

Pasteur has shown that easily fermented saccharine solutions can remain for years without decomposing, even when the air has access to them, provided that the living germs which were originally present in those solutions be first destroyed by heat, and that care be taken not to let any but absolutely pure, that is, germ-free air enter those solutions afterwards. But the moment impure air was allowed to enter the liquid, or the minutest portion of living yeast, fermentation was rapidly set up.

Pasteur has also shown that associated with ordinary yeast are to be found in most fermentations and beers a great number of organisms of quite a different appearance and character to yeast cells, and which may all be classed under the general term of bacteria, and he proved most

conclusively that these organisms are capable of and do give rise to the various diseases to which beer is subject. Or in other words, that, in addition to the healthy fermentation of saccharine solutions carried on by sound yeast, these other organisms, if present, are also capable under certain conditions of carrying on fermentations which give rise to products other than alcohol and carbonic acid. Hence these bacteria or false ferments have been classified and named according to the functions they fulfil or the products they give rise to.

Those organisms which induce alcoholic fermentations in a saccharine solution are known under the general name of saccharomyces, and since under normal conditions they reproduce themselves by gemmation or budding, they have been assigned to that division of the great fungus group known as budding fungi. In brewing technology they are known under the general term yeast. Yeast cells are either single or occur in groups or strings; each cell consists of a thin-walled sac or bag containing a semi-fluid matter, in the centre of which there is often a space full of a more clear and watery fluid than the rest, which is termed a vacuole. The sac is comparatively tough, but it may easily be burst, when it gives exit to its contents, which readily diffuse themselves through the surrounding fluid. The whole structure is called a cell, the sac being the cell wall and the contents the protoplasm. Under a high magnifying power each cell is seen to be round or oval, and on the average about  $\frac{1}{3000}$ th of an inch in diameter. An agglomeration of such cells is technically termed yeast, and to the naked eye appears as a thick slimy cream-coloured fluid, from which all the moisture can be pressed, and the residue dried at a low temperature to a powdery mass without losing its vitality; but if heated in the moist state to the temperature of boiling water, its fermentative power is completely destroyed. Fermentation which has already commenced in a saccharine liquid can be stopped by boiling it.

When a minute quantity of yeast is added to some malt wort which has previously been filtered bright, and is then kept in a glass flask at a temperature of about 70°F., after a few hours bubbles of gas will be seen to rise to the surface of the liquid, which gradually becomes more and more turbid, and later on a sediment will be observed at the bottom of the flask or a scum may collect at the surface, carbonic acid gas being copiously evolved. If the yeast cells be carefully examined under the microscope from time to time whilst this is going on, it will be noticed that at first the vacuoles which were present in every cell gradually disappear, each cell becoming full and rounded in appearance owing to the absorption through its cell wall of certain nourishing substances from the wort. Soon minute little buds will be noticed jutting out from the sides of the cells; these buds rapidly grow and soon assume the size of the parent cell, from which they finally become detached, but not before they in their turn have developed other buds, and these yet others, thus giving rise to those groups or strings of cells which are sometimes seen under the microscope. This cell reproduction and growth is due then to the nourishment which the yeast derives from the

wort, but for some time after the yeast cell continues to produce any buds, and even after the rupture takes place between the parent cells and the resulting daughter cells, the former still continue to absorb various substances from the liquid. This may be looked upon as a kind of fattening process, and is due to the assimilation by the yeast of certain nitrogenous matters contained in the worts. Hence, the process of fermentation of malt worts may be regarded as first an absorption of carbohydrate substance by the yeast cell, the transformation of this substance into alcohol and carbonic acid, whilst at the same time the oxygen derived from this decomposition enables the yeast cell to thrive and grow and to put forth buds.

When this period of growth is accomplished a fattening of the cells takes place at the expense of certain nitrogenous substances known as amides; if these be not present, no fattening takes place, and the yeast becomes starved, as it were, and perishes; if, on the other hand, there be a large excess of these nitrogenous matters in the worts, the yeast cells become overfed, and their capacity for reproduction considerably diminished, for it has been found that the power of multiplication and the formation of new cells decreases with the increase of nitrogen in the yeast.

As a matter of fact, a wort produced entirely from malt contains a very large excess of these assimilable nitrogenous substances, therefore it has been found advantageous by brewers to replace a certain proportion of the malt, generally  $\frac{1}{2}$  to  $\frac{1}{3}$ , by invert sugar or some other form of saccharine substance devoid of nitrogenous bodies.

Not only has Pasteur established the fact that fermentation is due to the development and growth of yeast in saccharine solutions, but he also has shown that there are several distinct species of yeast, each one differing from the other in functions and properties, and of the several species which are capable of inducing alcoholic fermentation he identified the following as being present in malt worts in addition to those species known as *Saccharomyces cerevisia*, the true beer ferment, *Saccharomyces pastorianus*, *S. ellipsoideus*, *S. exiguus*, and *S. apiculatus*. These he found were always present in the atmosphere as well as on the surface of all fruits, so that if some sweet wort be freely exposed to the air it will in the course of a few hours manifest all the signs of alcoholic fermentation; but, in addition to these various species of yeast, spores of bacteria and moulds will also manifest themselves and develop, so that after a few days, if left to itself, this wort becomes quite turbid, is covered with a thin film, emits a disagreeable smell, and soon putrefies. Hence the necessity for boiling the wort before fermentation; by this means all the spores which may have been present, derived in great part from the surface of barley or malt, are killed and the wort rendered free from all foreign germs, and ready to undergo a true yeast fermentation.

But although Pasteur has directed attention to the presence of these other forms of saccharomyces or wild yeasts, as they are now termed, in fermenting worts and beer, he does not tell us how to introduce into the liquid about to be fermented a seed yeast which is really free from all such forms of wild yeast. This work was

reserved for Hansen, and was brought to a most successful issue by him. He started with the idea of cultivating a crop of yeast from a single selected yeast cell, and pure yeast thus procured was first used for brewing purposes at old Carlsberg Brewery, near Copenhagen, in 1883 (Meddelelser fra Carlsberg Laboratoriet, 1881). Since then, carefully selected types of yeast from pure cultures on this method have been introduced into all the leading breweries of Denmark, Norway, and Bavaria, with the most marked success. So far, all the work that has been done with pure yeast relates to that particular variety which is employed on the Continent and known as bottom yeast or low fermentation yeast, so called because the fermentation is there carried on at a low temperature (47°F. or even lower), and is a slow process extending over some weeks, during which the yeast sinks to the bottom of the vats or casks, in contradistinction to the English method of fermentation termed high fermentation, and the yeast, top yeast, because here the process is conducted at a high temperature commencing at about 60°F. and running up to 70°F. or more, so that the fermentation is much more rapid and the yeast thus produced rises to the surface and works out of the bungholes of the casks or is skimmed off the surface of the fermenting tuns.

Nothing has yet been practically done in England on the large scale in the way of pure yeast cultivation, although several experiments have been made in this direction at Burton-on-Trent with different species of pure yeast, but there are yet many difficulties connected with the English system of brewing to be overcome, and from which our continental neighbours are exempt. However, 'sufficient has already been done to prove that in ordinary brewery yeast we (English brewers) also possess a mixture from which, by Hansen's method, several varieties of *S. cerevisiæ* can be separated, which cannot microscopically be distinguished from each other, but which when used upon a practical scale give entirely different results, both as to flavour, brightening, attenuation, and mode of separation of the yeast. Experiments have also shown that these characteristics can be maintained unimpaired throughout a very great many successive fermentations in the brewery' (Morris, S. C. I. 1887, p. 113).

Hansen found that particular forms of disease which manifest themselves in beers after it has been stored in cask are due to the presence of species of wild yeast (Meddelelser fra Carlsberg Laboratoriet, 1883), and notably to certain varieties of *S. pastorianus*, but he has also shown that if these wild types are present to the extent of not more than 2.5 p.c. on the total quantity of yeast, they do not develop their particular form of disease. Brown and Morris (Non-crystallisable Products of the Action of Diastase upon Starch, C. J. 1885, 569) have found that some of these 'wild types of yeast,' *S. pastorianus* and *S. ellipticus*, which with other species constitute the secondary ferments of our high fermentation beers, are capable of first hydrolysing the dextrin to maltose and then fermenting it, and these results have been fully confirmed by the author on the large scale in the brewery. It is perfectly certain that the 'sick frets' and other diseases which prevail in

summer time amongst certain kinds of beer, are due to the presence in large quantity of these wild yeast types in the beer.

As we have seen, the microscope does not enable us in some instances to differentiate one form of yeast from that of another, and in order to be able to do this some other method must be resorted to. It has long been noticed by many observers, more especially by Rees, Engel, and Brefeld, that under certain conditions the yeast cell, instead of throwing out a bud multiplies itself in another way, its protoplasm divides itself into four masses termed ascospores, each of which surrounds itself with a cell wall, and the whole are set free by the dissolution of the cell wall of the parent.

Hansen found that the ordinary bottom fermentation yeast only formed spores at 25°C. after some days, whilst the wild forms are capable of forming ascospores at this temperature in a few hours, and upon these results Holm and Poulsen (Meddelelser fra Carlsberg Laboratoriet, 1886) have based a method for the practical analysis of brewer's yeast. The method of procedure is as follows. A small quantity of the yeast to be examined is spread on a small sterilised block of plaster of Paris; this block is then placed in a flat covered glass dish and kept moist by water previously poured into the dish. This is then placed in the thermostat or forcing chamber and kept at a temperature of 25°C. for forty hours. At the end of that time it is carefully examined under the microscope, when the spores, if any wild yeast be present, will be seen as round bodies within the cell wall.

Yeast has always been classified as belonging to the fungoid group of plants, but those other organisms which also have the power of inducing fermentation other than alcoholic in saccharine solutions, have been regarded by the older observers as belonging rather to the animal than to the vegetable kingdom, chiefly on account of their motility and in the absence of the basis required for a more exact comparison, but later investigators see no reason for separating them from the vegetable kingdom, although all that can yet be said of them is that they may be classed as bacteria, and 'are a group of simple plants of a low order.'

Of these the species best known to us as occurring in beer are *Bacillus subtilis*, *Bacillus amylobacter*, *Bacterium termo*, *Bacterium aceti*, *Bacterium lactis*, and *Sarcina*. There are other species of which little is known, but which are often met with in old beer, such as the ropy ferment, colour bacterium, certain forms of *vibrio*, *spirillum*, &c.

These constitute what are known as the disease germs of beer, and generally develop under favourable conditions in the finished beer after it has been some time in cask or bottle: *Bacterium aceti* has the power of converting the alcohol of the beer into acetic acid, *B. lactis* attacks the saccharine matter, converting it into lactic acid, whilst butyric acid is supposed to be derived from the further fermentation of lactic acid by means of *Bacillus amylobacter*, or from sugar along with butyl alcohol by means of the same organism. These three forms of bacteria, along with *B. subtilis*, are perhaps those most commonly occurring in beer.



A few forms of mould are sometimes met with, such as *Mucor racemosus*, *Penicillium glaucum*, *Aspergillus niger*, but space will not permit to treat further of this subject.

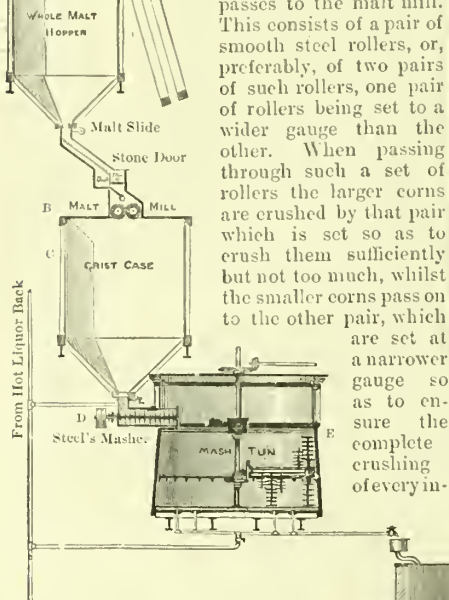
27. Having very briefly glanced at the different materials used in brewing, we proceed next to consider the various processes involved in the manufacture of beer.

**Preparation of malt for mashing.** As soon as the malt is delivered at the brewery it is further cleaned by screening from adherent dust, mould spores, and small

corns. It is then delivered into a small hopper, from which it passes to the malt mill. This consists of a pair of smooth steel rollers, or, preferably, of two pairs of such rollers, one pair of rollers being set to a wider gauge than the other. When passing through such a set of rollers the larger corns are crushed by that pair which is set so as to crush them sufficiently but not too much, whilst the smaller corns pass on to the other pair, which

are set at a narrower gauge so as to ensure the complete crushing of every in-

dividual corn. By this means a comparatively even grist is obtained. As the malt is ground it passes to the grist case (c, Fig. 8) which is generally placed over or has command of the mash tun.



dividual corn. By this means a comparatively even grist is obtained. As the malt is ground it passes to the grist case (c, Fig. 8) which is generally placed over or has command of the mash tun.

The grist case should be made of well-seasoned pine or deal, planed smooth and well jointed, and should be lined with sheet zinc, or it may be constructed of galvanised iron. The bottom of the grist case must be of sufficient slope to allow of the grist falling easily and readily into the mashing machine, and is provided at the bottom with a sliding valve.

28. **Mashing process.** From the grist case the crushed malt passes on to the outside mashing machine, where it meets with the mashing liquor at a temperature varying, according to circumstances, from 160° F. to 170° F. The malt and water are here thoroughly mixed before running into the mash tun. The best form of machine for this purpose, and the one most generally employed, is Steel's

masher, of which a section is shown at fig. 8. D. This consists of a horizontal cylinder closed at one end and open at the other, from 3 to 6 feet in length and from 8 to 22 inches in diameter. It is fixed horizontally above the level of the upper edge of the mash tun and is usually furnished with a shoot whereby the mash may be conducted into one or more tuns. For instance, where two mash tuns are employed, the steel masher is fixed between the two tuns in such a way that it can be used for either one at pleasure. Inside the cylinder and running its whole length is a shaft provided with spokes at short and regular intervals, and of such a length that they just revolve freely inside the cylinder as shown in section.

The shaft is driven by a pulley, and the grist is fed into the upper side through the upright T-piece, the water from the hot liquor back meeting the grist at this point.

A slide, accurately adjusted by means of a screw, regulates the fall of the malt, whilst a screw tap allows for the admission of the proper quantity of water.

The process of mashing is carried on in a vessel called a mash tun, E. This may be made of wood, wood lined with copper, or of iron, but the material most generally employed is wood. In this case it is constructed of staves of best English oak, with a bottom of Dantzic fir. The staves should not be less than two and a half inches thick for small tuns, which must be increased for larger tuns in proportion to their size. The mash tun is provided with a false bottom, an internal mashing machine, and a pipe, termed an underlet, for introducing hot liquor from the main into the mash tun when desired. The capacity of the tun should be such as to allow three and a half barrels for every quarter of malt to be mashed; to this must be added an allowance of 3 inches to the depth of the tun.

The false bottom, of such a thickness as to leave a space of two inches in depth between it and the real bottom of the tun, consists of a series of well-fitting stout sheet

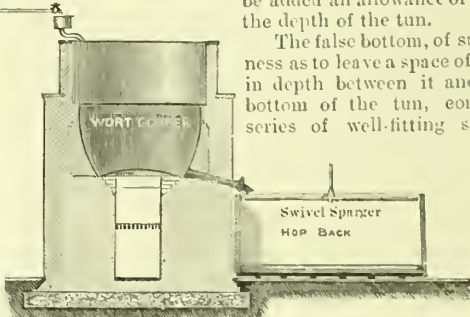


FIG. 8.

copper plates perforated with small holes or slots one-eighth of an inch in size and about one inch apart, and supported by wooden bearers. The internal mashing machinery consists of a horizontal shaft rotating at a level of about half the depth of the tun round a central vertical shaft as well as on its own axis, and fitted with light iron bars placed at regular intervals along the length of the shaft, which by their motion more effectually mix up the grist in the tun.<sup>2</sup>

One or more pipes, termed underlets, by means of which hot water can be introduced into the tun under the false bottom for the purpose of raising the temperature of the mash

<sup>1</sup> For the drawings of brewery plant the author is indebted to Mr. J. Oxley, Brewers' Engineer, Frome.

<sup>2</sup> For large mash tuns two such shafts are employed.

when required, should be affixed to every mash tun. This heating is termed *piecing up*, and the hot water run in for the purpose, *piece liquor*.

The relative proportions of a mash tun are a matter of some importance. The following table, given by Southby for the form of mash tun we are describing, shows these proportions as follows :

TABLE V.

Quarters of malt mashed	Diameter of tun	Depth of tun	Quarters of malt mashed	Diameter of tun	Depth of tun
	ft. in.	ft. in.		ft. in.	ft. in.
5	5 2	5 1	25	10 2	6 5
8	6 4	5 5	30	11 0	6 6
10	7 0	5 6	40	12 6	6 9
12	7 7	5 8	50	13 9	7 0
15	8 4	5 10	75	16 3	7 6
20	9 4	6 1	100	18 1	8 0

For the purpose of drawing off the aqueous extract of the malt, or in technical language

sweet wort, the bottom of the mash tun is provided with a suitable number of pipes, which should be attached at regular intervals to the bottom of the tun so as to ensure an equal draught from every portion. Of course the number of such draw-off pipes must vary with the size of the tun. A 25-quarter mash tun should have at least six draw-off pipes.

The mash tun in all instances is provided with a cover. This should be carefully made and should fit well ; it prevents the cooling of the mash and protects the surface of it from dust.

This cover may be of two forms, square top and conical, but the one to be most preferred is undoubtedly the conical. The square top, which is of the same diameter all the way up as the mash tun and is from two to two and a half feet in height, is provided with doors or sliding shutters. The great objection to this form is the large amount of space left above the mash,

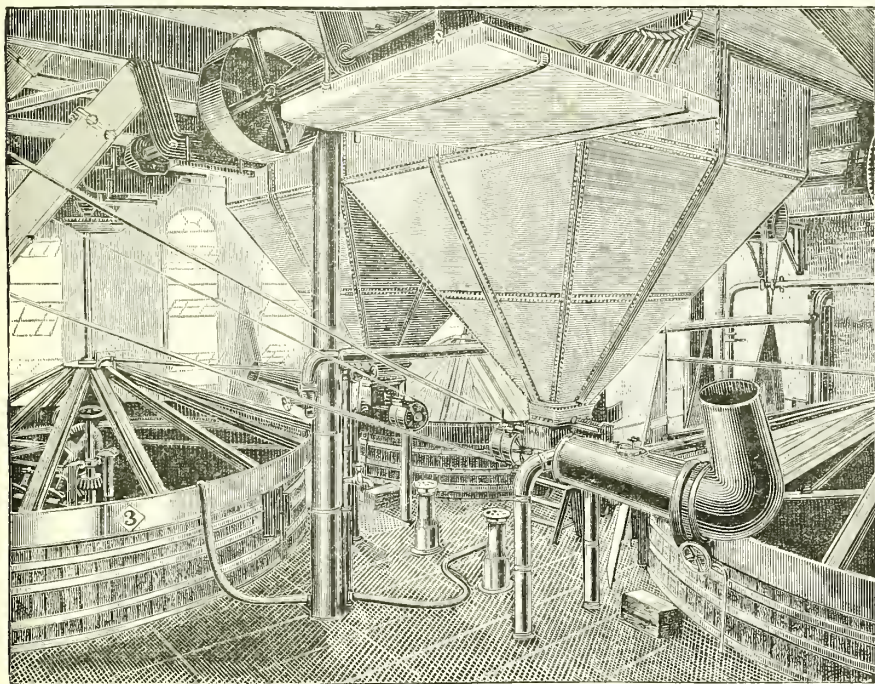


FIG. 9.—MASHING ROOM IN MESSRS. WORTHINGTON & Co.'s BREWERY, BURTON-ON-TRENT.<sup>1</sup>

and the facility afforded by the flat top for the collection of dust.

The conical cover is made in irregular sections, all of which are removable, whilst the objections to the square top are reduced to a minimum.

The draw-off pipes to which taps are affixed are carried separately from the mash tun to a small receiving vessel termed the 'underback,' into which the wort from each tap flows, and is conveyed from this to the copper.

Figs. 9 and 10 give a general view of all the mashing arrangements described above.

As we have said, the malt as it leaves the

grist case meets in Steel's mashing machine with the hot liquor, and both, thoroughly inter-mixed, are run into the mash tun. As soon as all the grist is run in, a few gallons of mashing liquor are run through the Steel's masher, and then the rakes are set going, two turns round the tun being considered sufficient. The temperature of the mash is then taken; this may vary from 140°F. to 150°F. according to the practice of the brewery. If this initial temperature is not up to the proper point, then some more hot liquor is introduced through the underlet until the right temperature is attained, the covers are shut up and the mash allowed to stand, generally for one and a half to two hours.

<sup>1</sup> This, with fig. 15, are taken from *Noted Breweries of Great Britain*, by kind permission of Sir J. Causton & Sons.



29. **The chemical changes which occur during mashing.** When ground malt is brought into contact with water at the mashing temperature, the starch which it contains becomes first gelatinised and then, in presence of certain albuminoid bodies collectively termed diastase, is rapidly dissolved and converted into dextrin and maltose; the other carbohydrates, such as cane sugar, dextrose, and levulose also enter into solution, as well as certain nitrogenous bodies termed amides. At the same time certain other nitrogenous bodies more or less insoluble in water are also acted upon by the diastase, becoming converted into peptones. There is also evidence that at least a portion of the cane sugar is by the same active agent transformed into invert sugar.

Recent researches have proved most conclusively that when gelatinised starch is acted upon by diastase it is split up into dextrin and maltose, and, under certain conditions, into maltodextrin as well, and that this change is a molecular one, and does not take place according to one equation but to several, depending upon the temperature at which such a transformation is effected, and that the conversion afterwards of the dextrins first formed into maltose is a slow and gradual act of hydration. In all probability the molecular transformations of starch may be represented by at least eight possible equations, depending upon the temperature at which such transformations are effected.

The following table gives the respective proportions of maltose and dextrin corresponding to these eight equations, as well as the cupric oxide reducing power  $K$  and specific rotatory power  $\{a\}_D$  (3.86 divisor), for the joint products of each of these transformations:

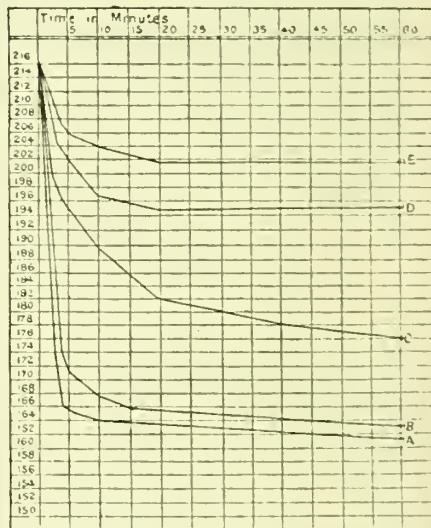
TABLE VI.

No. of Transformation	Maltose	Dextrin	K	$\{a\}_D$	Resulting Dextrin
Soluble starch	0	0	0	195.0	—
1	10.4	89.6	6.4	188.6	Erythro-dextrin $\alpha$
2	20.8	79.2	12.7	182.4	" $\beta$
3	31.0	69.0	18.9	176.2	Achroo-dextrin $\alpha$
4	41.3	58.7	25.2	170.2	" $\beta$
5	51.3	48.7	31.3	164.3	" $\gamma$
6	61.1	38.9	37.3	158.4	" $\delta$
7	71.0	29.0	43.3	152.5	" $\epsilon$
8	80.8	19.2	49.3	146.7	" $\zeta$
9	90.3	9.7	55.1	141.0	" $\eta$
Maltose	—	—	61.0	135.4	—

Throughout the whole range of the transformations of starch conducted with malt extract under the most varying conditions, results may be obtained which are always compatible with the hypothesis that the hydration and splitting up of the molecule of soluble starch are attended with the production of (1) a crystallisable body, maltose, having a specific rotatory power of  $\{a\}_D = 135.4$ , and a cupric oxide reducing power of  $K = 61$ , and (2) a series of non-crystallisable polymeric bodies, the dextrins, all having the same specific rotatory power of  $\{a\}_D = 195^\circ$  and no cupric oxide reducing power whatever.

The influence which temperature exerts upon the transformation is readily seen on referring to Table VII., where is shown a series of curves for transformations made under varying conditions of temperature, and taken from Brown and Heron's paper on the Transformations of Starch (J. C. S. 1879, p. 596). It is at once evident from these curves that the percentage of dextrin in any given transformation is directly proportional to the temperature, whilst on the other hand the maltose is inversely so. We are also struck with this remarkable fact, that with the exception of the transformation carried on at 66°C. (150.8°F.), the conversion of starch into dextrin and maltose, and the subsequent hydrations of the higher dextrins into the lower seem to be almost completed by the end of the first fifteen minutes, and even for the transformation at 66°C. there is a fall of angle of only 10° from fifteen to sixty minutes, whilst for the first fifteen minutes the fall is three times as much.

TABLE VII.



A. Transformations with unheated malt extract at 40°-50°C.; B. Ditto, heated to 60°C.; C. Ditto, heated to 66°C.; D, E. Ditto, heated to 75°C.

On the large scale in the brewery, where the process of mashing is carried on under the normal conditions, the transformation shown at 66°C. is the one which usually takes place.

This may be seen by referring to the curves shown in Table VIII.

These were deduced from a series of polarisations of worts from malt mashed under similar conditions—(a) in the laboratory, (b) in the brewery, water at the rate of two barrels per quarter of malt being used in both cases, and samples were taken every fifteen minutes from time of finishing mashing.

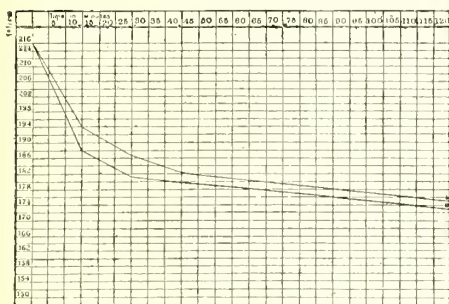
On comparing these with Brown and Heron's curve for starch transformations at 66° we are at once struck with the great similarity which exists between them, the nature of the curves being almost exactly the same in both cases, a comparatively rapid fall occurring during the first thirty minutes, slow and regular hydration



proceeding afterwards, but only to a slight extent, the difference in specific rotatory power between 30 minutes and 120 being only about 7° in each case, so that it may be taken for granted that the dextrin maltose ratio that is to obtain in the resulting wort is practically decided during the first thirty minutes. On comparing the curve at 66° in Table I. with those at higher and lower temperatures, it would appear, curiously enough, as if this temperature for mashing were just on the boundary line as it were, a few degrees either higher or lower giving worts highly dextrinous and poor in maltose, or else the very opposite.

Seeing then what a very great influence a few degrees of temperature would appear to exert upon the composition of the wort, too much stress cannot be laid upon the necessity of attending carefully to the initial temperature

TABLE VIII.



of the mash, and there can be little doubt that the polarisation of samples of wort taken, say, at fifteen, thirty, and forty-five minutes from time of finishing mashing, would give an intelligent brewer much valuable information as to the relative diastatic capacities of the several malts he may have to deal with, enabling him to form a pretty accurate idea as to the most suitable temperatures for future mashings, and giving him a more perfect control over the subsequent operations of sparging, pitching, attenuating, &c.

During the operations of sparging some of the harder portions of the starch which had hitherto escaped saccharification become dissolved out and transformed by the diastase still remaining into dextrin and maltose. If the sparging be applied at too high a temperature this starch becomes gelatinised, but, in great part unconverted owing to the destruction of the diastase at these temperatures, passes on into the wort, and although this starch of itself exercises very little if any injurious influence on the finished beer, it nevertheless serves as an index of other dangers, for the high sparging temperatures which bring into solution some of the previously unacted upon starch, also cause some of those nitrogenous bodies which at the ordinary mashing temperature are quite insoluble, to become partly soluble, especially in the presence of the saccharine matter of the wort; and these, finding their way in a state of semi-solution into the finished beer, cause a persistent cloudiness which neither finings nor storage can remove, besides offering encouragement to the develop-

ment of hurtful germs always present to a greater or less extent in freshly racked beer.

As soon as the mashing process is considered to be complete, the taps leading from the various underlets are opened, gently at first and afterwards more quickly, till the liquor runs half-bore and the wort is allowed to flow into the underback. The first few barrels that come over are generally cloudy, owing to the presence of small particles of the mash which have passed through the perforations in the false bottom, and partly from a reduction of temperature of the wort through coming in contact with the cold pipe. This cloudy wort is returned to the mash tun. As soon as the taps begin to run fairly bright the wort is allowed to flow from the underback into the copper.

When the mash is completed and the wort is running into the copper, the temperature of the liquor, or tap heat, as it flows from the taps is taken. This is generally done about half an hour from time of first setting taps.

**30. Sparging.** After a certain number of barrels of wort have been drawn off, a further quantity of mashing liquor is sprinkled over the goods by means of a sparger, for the purpose of washing out as completely as possible the wort still adhering to the insoluble matter or grains in the mash tun. The sparger (fig. 8, e) consists of two or more hollow arms perforated along one side and extending to the sides of the mash tun. They are connected with a central basin through which the upright shaft of the mashing machine passes, and the basin runs on wheels fixed to a carriage on the upright shaft. The mash liquor flows into the central basin, thence along the arms and through the perforation, causing the arms to revolve; by this means the whole of the goods are exposed to a washing operation, whereby the greater part of the residuary wort matter adhering to the grist is abstracted. Most brewers begin sparging shortly after setting taps, and keep the sparges going continuously until the whole of the wort matter has been got away from the grains; others do not commence to sparge until one-fourth, one-half, or even three-fourths of the strong liquor has been drawn off. It is preferable to start sparging when the first ten barrels of wort are in copper, at the rate of one-half to three-quarters of a barrel per quarter of malt, at a temperature of 170° F., and until the upper layers of the mash, which have begun to cool somewhat, are again at the normal temperature, the sparging liquor is then cooled to 160° F. and the sparging carried on continuously at this temperature until the copper is made up. If higher temperatures than these are used a risk is incurred of dissolving out some of the unaltered starch, of which there is always to be found a small portion remaining in the grains and which has not been acted on by the diastase of the malt.

When the gravity of the wort running from the taps has fallen to about sp. gr. 1005, it is advisable to shut off the taps.

**31. Boiling.** As soon as the wort leaves the mash tun it is, as we have already seen, either run directly into the copper or collected first in an intermediate vessel called the underback, but it is advisable that it should remain only a short time in this vessel so as to prevent any appreci-

able loss of heat. As soon as the first ten barrels are in the copper the fire may be got up, and the temperature of the wort raised to about 180° F. or 190° F. At the same time a certain proportion of the hops may be added—for instance, for a 100 barrel copper a tenth portion of the total hops should be added, and for every ten barrels of wort added a tenth part of hops, and so on until all the wort is run into the copper or the copper is made up. As soon as the last tenth of the hops is added the fire is increased and the wort brought to the boiling-point as quickly as possible. This is carried on usually for one and a half to two hours.

In some breweries it is the custom to keep the wort as it flows into the copper at a temperature not exceeding 165° during the time the copper is being filled. This process is called stewing the worts, and is said to be often very advantageous, especially when the malts are deficient in diastatic power. No advantage can possibly accrue from such a process, but, on the contrary, much harm may result therefrom to the finished beer. With regard to the period at which it is most advisable to add the hops, much difference of opinion exists, some brewers not adding any until the copper is nearly or entirely made up, others adding the whole of the hops before the

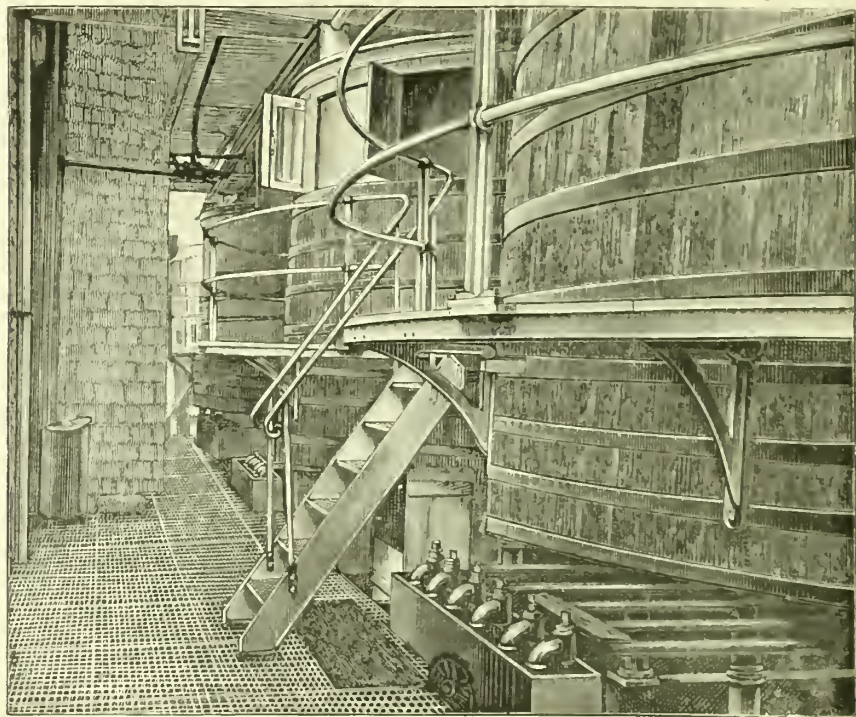


FIG. 10.—MASHING ROOM, ANGLO-BAVARIAN BREWERY, SHEPTON MALLET.

copper is half full. Both methods are very objectionable; the addition of the hops to the copper ought to run *pari passu* with the inflowing wort. By this means we get a more regular precipitation and coagulation of certain albuminous substances from the wort, and a more even extraction of the bitter and resinous principles of the hop, the result being a well broken, regular wort and superior flavoured beer. A favourite plan in many breweries, and one which for several reasons is to be strongly recommended, is to reserve the last tenth part of the hops, and which should be of superior quality to the rest of the bulk, until about ten to twenty minutes before turning out the copper, the effect of this being to give a certain amount of aroma and hop flavour to the wort, and which enables the objectionable practice of dry hopping to be dispensed with. We have assumed that the whole of the wort from one brewing is boiled at once in one copper, and, where practicable, this is by far

the best plan; but more often the wort from one brewing is divided between two coppers, the stronger wort being boiled in the first copper with the whole or greater part of the hops, whilst the last half and weaker portion of the worts is run into the second copper and boiled with the already exhausted hops which are returned from the first copper. This is a very objectionable as well as dangerous method of procedure. The first copper wort will contain proportionately much more saccharine than nitrogenous matter, the latter being in excess in the second copper; again all the tannin and the largest proportion of the soluble matters are extracted from the hops by boiling them in the first copper, so that when these hops, which are practically exhausted of all their useful properties, are added to the second copper of wort containing relatively more albuminous matter than the first, comparatively little precipitation or coagulation is produced by the matter ex-



tracted from the hops, whilst a nasty, coarse, bitter flavour is imparted to the wort, so that the resulting beer contains an excess of nitrogenous matter, thereby being rendered more liable to disease, and brightening only with difficulty. Where it is necessary to divide the wort between two coppers, the stronger wort may be run into one and the weaker into the other, but to both coppers fresh hops should be added in quantities proportionate to the gravities of the respective worts.

During the boiling of the wort with hops in the copper, all diastatic action is completely destroyed, and the starch products become fixed, a large proportion of the hitherto soluble albuminoids are precipitated, whilst a small quantity of hop extract is added; at the same time a slight alteration occurs in the carbohydrates other than those derived from the starch, being probably due to a slight inversion of a part of the unacted-on cane sugar by the acid of the boiling wort, but practically, the actual composition of the starch products is unaltered during the boiling process, so that the wort at this stage affords a very good index as to the dextrin percentage of the resulting beer, and hence a systematic polarimetric examination of wort from the copper will be found to be extremely useful. It may be taken as a general rule that the specific rotatory power of a wort should not fall below  $105^{\circ} [\alpha]_D$  or rise higher than  $122^{\circ} [\alpha]_D$ , the former indicating an abnormally low percentage of dextrin and large excess of soluble nitrogenous matters, the latter a very high percentage of dextrin resulting probably in extremely high attenuations and cloudy beers, fining only with difficulty.

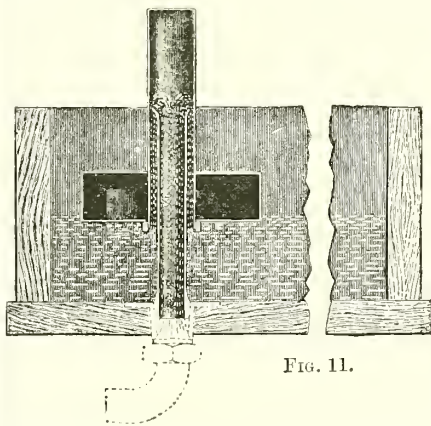
When the boiling process is completed the wort with the hops is run out of the copper into the hopback. This is a vessel of somewhat similar construction to the mash tun; the sides may be square or circular in shape, preferably the latter, and is furnished with a perforated copper false bottom. Here the wort is drained from the hops and run into a small wooden underback, whence it is pumped up on to the coolers, but as the hops in the hopback retain a certain proportion of the wort adhering to their surface, boiling water is sparged over them, and these spargings are added to the wort and serve to reduce it to the required gravity. Where brewing sugar of any description, whether cane sugar, invert, or glucose, is used in the brewing, it is best to add the requisite quantity previously dissolved in boiling water to the wort in copper about fifteen minutes before turning out; the usual proportions are from one-third to one-fifth of the quantity of malt used, 2 cwt. of sugar being reckoned to be equivalent to the extract yielded by 1 quarter of malt. The quantity of hops used will of course vary with the gravity as well as quality of the wort. In Burton as much as 20 lbs. of hops per quarter of malt have been used for export pale ales, but for ordinary pale ales from 10 lbs. to 15 lbs. is the usual proportion, less being required where malt substitutes such as invert sugar or glucose are used.

Of late years the practice of boiling the worts in wooden backs by means of steam at high pressure has been introduced into certain

breweries, and is strongly advocated by some brewers as being superior to boiling by fire. Boiling by steam certainly entails less labour, but there can be no doubt that if a brewer wishes to produce a beer that will keep sound for any length of time, the wort must be thoroughly well boiled so as to completely coagulate and fix all changeable albuminous matters as well as destroy all spores of disease germs, and for this purpose it is capable of proof that direct fire heat is much more potent than steam heat.

**32. Cooling.** Coolers may be described as large shallow tanks about eighteen inches deep, of such capacity as to contain the whole contents of the copper at one time; they are generally constructed of wood, but wood lined with sheet copper is much to be preferred, being far less liable to retain any contamination in the way of spores of bacteria or mould.

The principal object in running the wort on to the coolers is undoubtedly to lower the temperature or to take the 'fire heat' out of it; but at the same time another action is going on, the importance of which has only been clearly understood during the last few years, and that is the aeration of the wort or the absorption by the wort of the oxygen of the air, either by way of solution or of combination, for not only does the atmospheric oxygen become dissolved in the wort in a manner similar to carbonic acid in water, but it actually enters into direct chemical combination with certain nitrogenous constituents of the wort, rendering them thereby insoluble and causing such substances to be



deposited on the coolers. Aeration has also a considerable influence on fermentation, indeed 'in the ordinary process of brewing normal fermentation would be almost impossible, and in every case most defective, if the wort, before being run into the fermenting vessels were not aerated by its passage over the coolers, where the aeration is more or less effective according to the depth of liquid on the coolers.' It is evident then that it is decidedly advantageous to allow the wort to remain a certain time on coolers before passing it on to the fermenting rounds, and also that the surface liquid should be drawn off first. This has been effected in a very ingenious manner by the arrangement shown in



fig. 11, which is the invention of Mr. S. Briggs, of Burton-on-Trent.

This apparatus simply consists of a vertical tube made of metal, fixed over the outlet of the cooler or vessel.

When the wort or other liquid is ready to be run off, the tube is filled with liquor, the float placed over the tube, and the outlet tap opened; the wort or liquid at once begins to run over the

down first, so that the whole or greater part of the sediment is left on the cooler.

It likewise gets a bright wort down over the refrigerator into the fermenting tuns, for while the bright wort is running off from the top, the grounds and thick sediment sink to the bottom, and remain on the coolers.

After leaving the coolers the wort, which is not yet by any means cold, is passed over a refrigerator, where it takes up in its passage a still further quantity of oxygen. There are several forms of refrigerators; the vertical one such as shown in fig. 12 is generally considered the best.

These refrigerators are made from seamless copper tubes, with a rib or feather on bottom and groove or channel on top side, running full length of tube. The rib or feather of one tube is securely fastened into the groove or channel of the next tube, thus giving great solidity, and presenting an even surface to prevent any liability of dirt accumulating, the brewer being able at a glance to see if the machine is perfectly clean.

The ends are fitted with gun-metal boxes with movable caps, giving easy access for brushing out the tubes, and are especially adapted for pumping, the tubes having no divisions to impede the water passage.

They are fitted with adjustable feet for regulating the flow of wort, and a perfect capillary attraction is obtained, a great desideratum in vertical refrigerators. The inlet trough is divided to secure an equal flow of wort down both sides of the machine.

But all the time that the wort is on the coolers and refrigerator it is exposed to danger of contamination with germs of disease such as

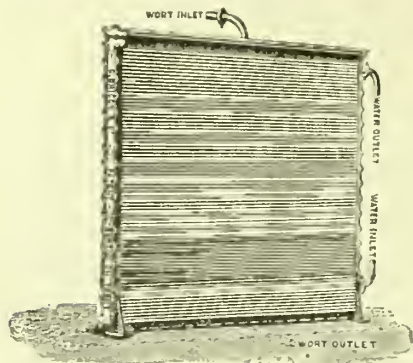


FIG. 12.

top of the tube and continues doing so until the whole is run off from the cooler or vessel.

The supply of liquor always being taken from the top, the brightest and coolest wort is run

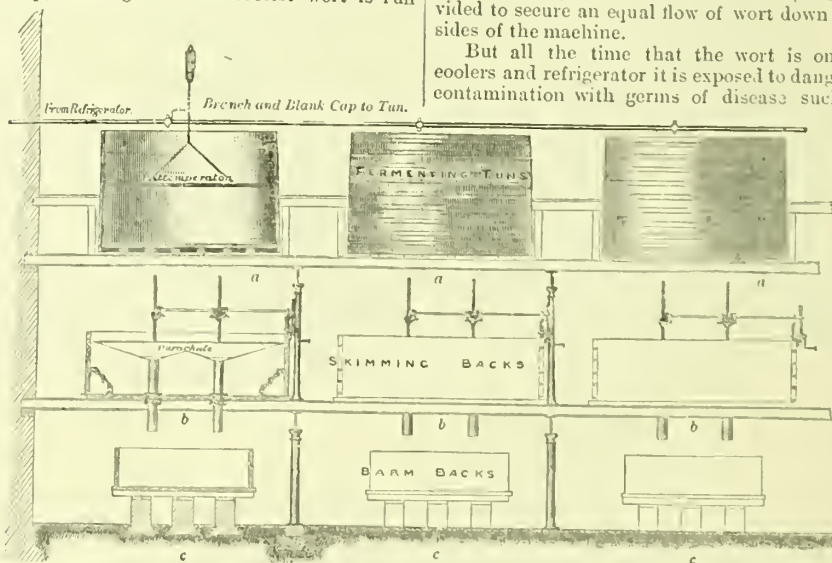


FIG. 13.

baacteria and wild types of yeast which are to be found always floating about in the air. Also beyond a certain limit aeration is injurious to the palate characteristics and aroma of the finished beer, hence it is advisable that consistently with sufficient aeration the wort should be cooled as quickly as possible, especially when it reaches a temperature of 150° and lower. Coolers and refrigerators should therefore be of sufficient capacity to cool the whole of one brewing or gyle

down to the required temperature, 58° to 60° F., in at least six hours, counting from the time the first of the wort is pumped on to the coolers until the last of it is in the fermenting vessel. This temperature will vary slightly with the quality of the wort and the temperature of the atmosphere, but for beer of medium strength, and where the atmospheric temperature is about the average, 58° to 60° F. in winter and 58° F. in summer may be taken as safe temperatures

for cooling the wort to, previous to adding the yeast.

**33. Fermenting.** From the refrigerator the wort is conveyed by copper pipes to the fermenting tun (fig. 13, *a*). This is usually constructed of wood, and may be square or round, preferably the latter, as being more easily cleansed. The wood generally preferred is Dantzic deal, but care must be taken before using vessels made with this wood to first remove the resinous flavour from it before running in the wort. The fermenting round is furnished with an attenuator or coil of pipe through which either hot or cold water may be transmitted for the purpose of regulating the temperature of the fermenting wort. As soon as the first ten barrels of wort are in the fermenting tun the requisite quantity of yeast may be added; this is called 'pitching.' The quantity of yeast to be added will of course vary according to the strength of the wort, the quantity of hops used, quality of yeast, and season. For light ales and running beers about  $\frac{3}{4}$  lb. to  $1\frac{1}{2}$  lbs. per barrel of wort are used, whilst for the stronger ales from  $1\frac{1}{2}$  to 3 or even 4 lbs. in some cases are used.

In general appearance the yeast should be of a rich cream colour, possessing a sweet clean smell. Under the microscope the cells should be uniform in size, full and plump-looking, and transparent, containing few, if any, vacuoles or granulations; the cell walls should be thick and free from pittings, and stand well out against the field. No signs of budding should be apparent, and no dead or shrivelled cells should be present. The presence of any dead cells may easily be determined by running on to the slide a drop of methylene-blue solution, which *instantly stains all dead matter, but has no effect on living cells.* In a really good pitching yeast no bacteria or other germs of disease ought to be present, but most yeasts generally contain a few. As a rule any sample of yeast that contains more than 20 short bacteria (rods) in 10 fields ought to be condemned for pitching purposes; the presence of any of the longer forms of bacteria, whether straight or bent, is sufficient to at once condemn the yeast as being a highly dangerous one to use.

As has already been mentioned, it is almost impossible to determine by ordinary microscopical examination the presence or absence of wild types of yeast; these must be looked for by Hansen's method of ascospore formation.

As soon as the wort has been cooled to the proper temperature, and ready to undergo the process of fermentation, it is, according to the Inland Revenue Act of 1880, run into a vessel called the collecting vessel, where it must remain for a period not less than twelve hours, or until such time as the excise officer can determine its gravity and bulk for the purpose of levying the required duty. In most breweries these collecting vessels are the fermenting tuns themselves.

After all the wort has been run into the tun and the yeast thoroughly roused up with it, the process of fermentation commences; bubbles of gas rise to the surface until, after a while, the whole of the surface becomes covered with a creamy froth. As the fermentation progresses

and the decomposition of the sugar becomes more rapid, the greater is the amount of carbonic acid which is liberated, and the froth swells up to such an extent that at last, not being able to resist any further tension, it topples over, giving rise to that 'rocky' appearance which is seen on the surface of healthy fermentations during the earlier stages. At the same time the temperature of the liquid will be noticed to rise steadily. If this goes on too fast it must be checked to a slight extent by running some cold water through the attenuator. Under normal conditions a rise of  $1^{\circ}$  ought to take place in six hours, so that at the end of about sixty hours the temperature of the fermenting wort would have risen to  $70^{\circ}\text{F.}$ ; the beer will at the same time have attenuated to about one-half. Thus a beer wort which had a specific gravity of 1050 at time of pitching will now show an apparent specific gravity or attenuation of about 1023.

This is about the highest point the temperature is allowed to rise to. When therefore this point is reached, the separation of the yeast from the beer, or the cleansing process, is commenced.

Up to this stage from the time of pitching, the fermentation is very closely watched by the brewer, and the temperature and attenuation taken at intervals of about five hours. If the fermentation goes on too rapidly it is easily controlled by running more water through the attenuator.

When the yeast is first added to the wort it lays hold of the free oxygen which has been dissolved by the passage of such wort over the refrigerators, and not until the greater portion of that oxygen is used up do the yeast cells begin to attack the sugars of the wort and split them up into carbonic acid and alcohol. It has been found in practice that the fermentation proceeds more satisfactorily if a certain amount of aeration is carried on during the process. This can be done by pumping air into the tun of fermenting wort, but yeast not only requires a limited amount of air, but also a vigorous motion from time to time, in order to enable it to do its work effectually as well as to render it capable of being eliminated from the beer. Hence a thorough rousing by means of long paddles or oars worked with hand, or by some form of the various machines introduced for this purpose, is necessary at stated intervals, more especially where the fermentation is inclined to be at all sluggish.

**34. Cleansing.** The separation of the yeast from the beer may be accomplished in many ways, the three principal systems are known as:

The *cleansing system*, as practised in some London breweries, and also in Burton, but on a very much improved method.

The *skimming system*, as generally adopted throughout the South and West, as well as many other parts of England, and

The *stone square system*, which is almost exclusively confined to Yorkshire.

In London and indeed in many country breweries the cleansing is effected by running the beer from the fermenting tun by means of a hose into ordinary 36-gallon casks, arranged

in rows side by side on a wooden trough or stillion, about two feet from the ground. The beer remains in these casks for some days, the bung-hole being left open, and through it the yeast works out and falls into the stillion. As the yeast works over, more beer is added to each cask, so that by the time the beer is freed entirely from the yeast, each cask is full and ready to be bunged up, and sent away for consumption, for London beer fermented upon this system is generally drunk within a week. This method of cleansing is, however, being rapidly replaced by the skimming system; this in principle simply consists in skimming off the yeast from the surface of the liquid from time to time as it rises to the top, and may be effected either in the fermenting tun itself, or, which is much preferable, in the cleanser. The beer, when it has attained the proper degree of attenuation and temperature, is run down from the fermenting tun along with the yeast into a large square

wooden tank called the skimming back or settler (fig. 13, *b*). This is fitted with attenuators which run round the sides; at one end are fixed two parachutes, which are simply large flat funnels of copper having pipes 4 inches in diameter attached to them, the whole being tinned over, and capable of being raised or lowered at pleasure by means of a screw and winch handle.

When the liquor is run into the settler, owing to the thorough aeration which it receives in so doing, a vigorous fermentation takes place, and unless carefully watched the temperature is apt to rise. At this point attenuation must be attended to, but the fermentation must not receive too severe a check. Soon a film of yeast mixed with carbonic acid gas appears on the surface of the liquid, which gradually gets thicker, so that about 6 hours after running or running into the cleansing tank, the first head of yeast is ready to be skimmed off. This is done

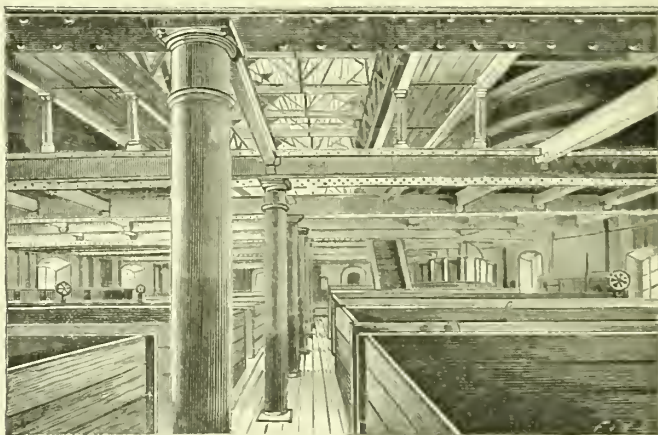


FIG. 14.—TUN ROOM AT ANGLO-BAVARIAN BREWERY, SHEPTON MALL.

by means of a plank as long as the tank is wide, furnished with handles, and held vertically by two men at the end opposite to the parachutes, in such a position that one end of the plank just touches the surface of the liquid immediately beneath the head of the yeast. This plank is then gradually moved along the length of the tank, pushing the yeast before it. The parachutes are fixed so that they will just receive the yeast which overflows into them, which is then conveyed into slate tanks placed immediately beneath (see fig. 13, *c*). Here it is allowed to remain for some hours, being roused occasionally so as to drive off the carbonic acid gas as well as to enable the beer which has come over with it to settle out, and which is drawn off through a tap at the bottom of the tank. The yeast is either pressed and sent away, or used for pitching fresh wort.

After the first skimming the yeast still continues to throw up a cleaner and whiter-looking head, so that in about three or four hours' time a second skimming is made, and so on every three or four hours until all of the yeast has separated from the beer. It is generally found that from four to five skimmings are necessary to effect this. After the last skimming a thin

but tough film of yeast forms on the surface; this is allowed to remain, and serves as a covering to protect the beer from aerial contamination and from oxidation, as well as to prevent the escape of carbonic acid. A general view of these skimming backs is shown in fig. 14.

It usually remains from two to three days in the settlers after the last skimming, so as to allow all matters in suspension to settle out.



FIG. 15.

At the end of that time the beer, which is now very nearly if not quite bright, is run down into a large tank, termed a racking square, where, after remaining a few hours, it is racked off into trade casks, either to be sent away for consumption or to be stored for some time to mature.

The Burton Union system, as the Burton



system of cleansing is called, may be regarded as the scientific development of the old London system of cask cleansing on stillions. In this system a number of casks or unions (fig. 15) capable of holding four barrels of beer, are placed side by side in two rows; these are hung in sets of twelve or more on a substantial frame, so as to admit of a free revolution of each cask on its axis, so that when the casks are to be washed they can be filled with boiling water, bunged up, and rapidly revolved. Supported on the same frame, and immediately above and running parallel with these rows of casks, is a long shallow trough called the yeast trough, and at one end and at right angles to it is another trough called the feeding trough. From this trough a pipe, two inches in diameter, runs

along the whole length of the series of casks on either side, and is connected with each cask by T-pieces and screw unions. At the highest part of each cask is fixed a ground brass socket, into which is fitted a peculiarly shaped pipe of tinned copper, termed a swan-neck, which is arranged to bend over the yeast trough, and serves to convey the yeast thrown off during cleansing to this trough. In order to keep the casks full a certain quantity of wort is placed in the feeding trough, which is allowed to run into the casks from time to time to replace the yeast (and beer carried over with the yeast) which has worked over into the yeast trough. After a time the beer carried over with the yeast separates out and is allowed to flow into the feeding trough through a series of holes in the end of the yeast

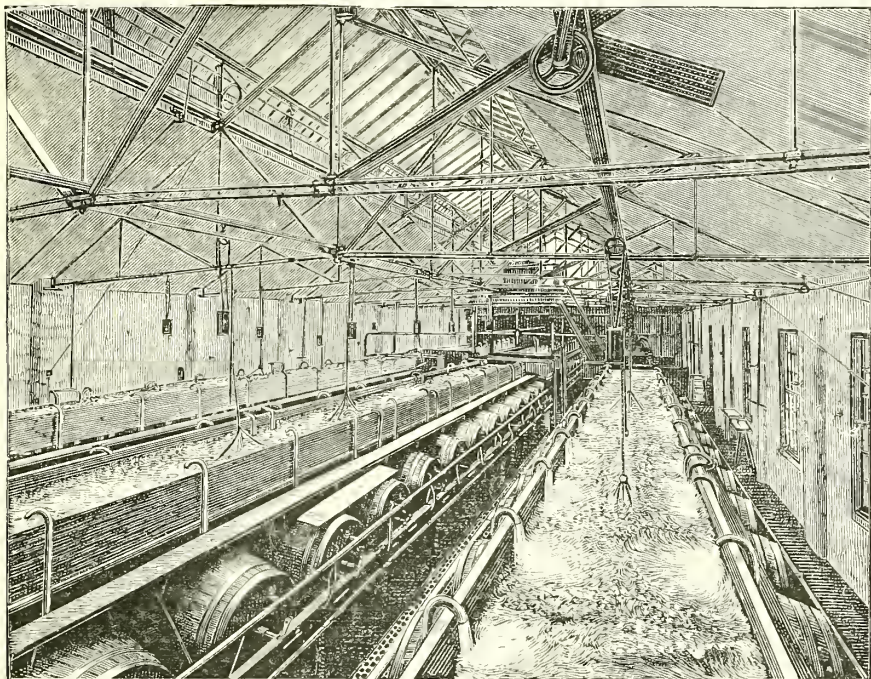


FIG. 16.—UNION ROOM AT MESSRS. WORTHINGTON & CO.'S BREWERY, BURTON-ON-TRENT.

trough nearest to the feeding trough, of which it forms one of the sides; these holes are closed with corks, and the man in charge ascertains by trial at which holes the beer will run off free from yeast, and accordingly opens these in turn so that the casks are always kept more or less full of beer. This feeding or sparging is done at intervals of three hours until the active fermentation has ceased. After the fermentation has subsided, and no more yeast is observed to come over, the swan-necks are removed, the casks bunged up, and the contents allowed to remain at rest for a few days longer for the purpose of allowing any yeast or other matters that may have remained in suspension to settle down to the bottoms of the casks. The clear ale is then drawn off by means of a screw tap fixed at the lower part of each cask. The tap projects six inches upward into the cask, so as to prevent

the sediment or grounds from being drawn off at the same time as the clear liquor. From these taps the finished beer is delivered by means of a trough running underneath them into a large settling back or racking vessel, where it is allowed to settle for a short time before being drawn or racked off into trade casks.

Where the Union system is employed no attenuators whatever are used in the fermenting tuns, the time for the beer to be tunned being regulated entirely by the temperature. As soon as 70° is attained the beer is immediately run into the unions. Neither are any attenuators used in these casks in winter, but during the summer months free recourse is had to attenuating. Fig. 16 gives a very good idea of the Union system of cleansing.

Space will not permit us to enter into a detailed description of the various other systems

of fermentation carried on in this country, and we must now pass on to treat very briefly of the German system of beer-brewing.

The German or decoction method of mashing is generally carried out as follows:

Ground malt is run into the mash tun, in which are two-thirds of the required water at the ordinary temperature of the air; here it remains for two hours. In the meantime the remainder of the water is heated to boiling in the copper, and then run slowly into the mash tun, the rakes at the same time kept revolving at a good speed. By this means the temperature of the mash is raised to 95 F.-100 F. The first thick mash (about one-third of the whole) is now drawn off into the copper and boiled for thirty minutes, and then returned to the mash tun, the temperature of which is thus raised to 116 F., the rakes being kept going during the addition of the first boiled mash. A second thick mash is now drawn off into the copper and heated to boiling-point, and kept boiling for fifteen minutes, and then run back again to the mash tun, the temperature being now raised to 149 F. After this the clear part of the mash is run off and boiled in the copper for fifteen minutes and run back again to mash tun; the temperature of the mash is now 167 F. The mash is now covered up, and allowed to lie for one to one and a half hours; the taps are then set, and the clear wort boiled for two hours with hops at the rate of about 2½ lbs. of hops to every 100 lbs. of malt used. The wort is then drawn off and run over coolers and refrigerator, where it is cooled down to 40 F., and thence to fermenting tuns, which are generally placed under ground in order that they may be kept cool by ice; and for that purpose small fermenting vessels of about twenty barrels capacity are used. These are filled nearly full with the wort, and bottom yeast in the proportion of about 1 lb. to every 5 barrels of wort added; the yeast, previous to being added to the wort, is first mixed with some wort of the former day's brewing, and thoroughly aerated by repeated pouring from one vessel to the other, and then put aside in a warm place for some hours, so that by the time the wort is ready to be pitched a lot of new and vigorous yeast cells have already formed and the fermentation is well started. During the earlier stages of fermentation a slight head rises to the surface; later on the yeast deposits on the bottom of the fermenting vessels. During this primary fermentation, which lasts about twelve days or more, the temperature of the fermenting wort is kept at about 44 F. When the primary fermentation is finished the attenuation has run down to about one half the original gravity of the wort, and the beer is run off, as free as possible from sediment, into casks, ranged in tiers on either side of large cellars, which are kept cold by ice. Here they are allowed to remain for some months, during which time a secondary fermentation goes slowly on, and the beer gradually clears itself until it becomes brilliant and fit for use.

Where beer is required for quick consumption it is usual in order to enable it to become bright rapidly to add a solution of isinglass, or 'finings' at the rate of 1 to 4 pints or more per barrel of beer.

The isinglass unites chemically with the tannic acid which is nearly always present in beer, forming a gelatinous flocculent precipitate of tannate of gelatin; this very soon sinks to the bottom of the cask, carrying all matter in suspension with it and leaving the beer clear and brilliant.

Finings are generally made by dissolving isinglass in sour beer. This is a crude and dangerous method. In the first place the isinglass takes several weeks to dissolve, and secondly, by means of this sour or turned beer a great risk is run of introducing into the sound fresh beer all kinds of disease germs, but more particularly *S. pastorianus*, as well as the ropy and lactic ferments.

The best and purest finings are undoubtedly made by dissolving good isinglass in dilute solution of sulphurous acid, and on no account should any other kind of finings be used in the brewery.

Beer which is not required for immediate use is stored in cellars at a temperature of 54 F., either in vats or in the casks in which it is to be sent out. Such beers are generally not fined, and each cask is furnished with a porous spile or vent peg to allow of the escape of a portion of the carbonic acid produced, owing to a secondary fermentation which always sets up in casks when beers are stored for any time.

Chemical analysis of a beer should be made shortly after racking, and before the secondary fermentation in cask has commenced. Such an analysis, calculated on the solid extract of the original unfermented wort, will show

- a. Matter fermented, p.e.
- b. Maltose unfermented.
- c. Dextrin unfermented.
- d. Albuminoids, ash, &c.

As the character and keeping properties of a beer depend to a very large extent on the percentage of unfermented dextrin which it contains, it would appear very desirable that an analysis of those beers required for stock or export should occasionally be made, so that an idea may be obtained as to the constancy or otherwise of their composition, and hence their suitability for the purpose for which they were intended.

Generally, at time of racking, and indeed in some cases at different stages of the brewing process, some form or other of antiseptic is added to the beer for the purpose of protecting it against the germs of disease to which from one cause or another it is so subject. The substances most generally employed for this purpose are calcium bisulphite and salicylic acid. Lately a particular form of potassium sulphite, known as kalium metasilphite, has been introduced for this purpose. The antiseptic, whatever it may be, is added either to the beer whilst in the racking square or to the beer in cask just after racking, if calcium bisulphite, at the rate of  $\frac{1}{4}$  to  $\frac{1}{2}$  pint per barrel, or salicylic at the rate of  $\frac{1}{4}$  ounce or less per barrel.

Experience shows that calcium bisulphite is much to be preferred to salicylic acid, but the chief objection appears to be the smell which it sometimes imparts to the beer, especially when used in any quantity. This may be got over by using kalium metasilphite instead, which is



claimed by the discoverers to be much more powerful in its action than bisulphite, whilst it imparts no smell to the finished beer.

Absolute cleanliness in every part of the brewery and in every portion of the plant is necessary, for unless due regard be paid to this point, no matter how good the materials or how perfect the process of manufacture, the quality of the finished article will be sadly defective in its most vital characteristic, viz. keeping properties; false ferments and micro-organisms of all kinds will be taken up by the beer at all stages of its manufacture, rendering it after a time sour, unpalatable, and unfit for consumption. In order to obviate this, every portion of plant, when not in use, should be thoroughly well cleansed and disinfected with suitable agents, such as chloride of lime, calcium bisulphite, caustic potash, &c., but for full details on this important question the reader is referred to a most valuable paper by A. Hartley in the *Trans. of the Laboratory Club*, 1, 42. J. H.

**BRIDELIA BARK** or **ASDUANA**. The bark of *Bridelia montana* is a useful Indian astringent (*Dymock*, P. [3] 7, 309).

**BRILLIANT COTTON BLUE** *v.* **TRIPHENYLMETHANE COLOURING MATTER**.

**BRILLIANT CONGO** *v.* **AZO-COLOURING MATTERS**.

**BRILLIANT CROCEIN** *v.* **AZO-COLOURING MATTERS**.

**BRILLIANT GREEN** *v.* **TRIPHENYLMETHANE COLOURING MATTERS**.

**BRILLIANT ORANGE** *v.* **AZO-COLOURING MATTERS**.

**BRILLIANT PONCEAU** *v.* **AZO-COLOURING MATTERS**.

**BRILLIANT SCARLET** *v.* **AZO-COLOURING MATTERS**.

**BRILLIANT YELLOW** *v.* **AZO-COLOURING MATTERS** and **NITRO-DYES**.

**BRIMSTONE** *v.* **SULPHUR**.

**BRINDONIA INDICA**. A plant belonging to the order *Guttifera*. The pericarp of the fruit is used at Goa as a spice and the blood-red acid juice as a lemonade. The seeds yield 30 p.e. of fat, which contains 50 p.e. of stearic acid. The cake left after the removal of the fat contains a fine red colouring matter soluble in water and alcohol (Bouis a. Pimentel, C. R. 44, 1,355).

**BRIQUETTES** *v.* **FUEL**; also **PITCH**.

**BRITANNIA METAL**. Is an alloy of variable composition, usually containing only tin and antimony, although brass and bismuth are sometimes added.

An alloy consisting of 9 parts of tin and 1 part of antimony is attacked slightly by solutions of common salt, potassium ammonium, and magnesium chlorides, potassium sulphate, potassium nitrate, and sodium carbonate. Caustic soda has a more marked action (D. P. J. 221, 259).

This alloy is used in the manufacture of teapots, spoons, and dish-covers.

Articles made from it may be coloured by heating them for 15 to 30 minutes in a bath made by mixing 2 lbs. of water,  $1\frac{1}{2}$  oz. of cream of tartar,  $\frac{1}{2}$  oz. of tartar emetic, 2 oz. of hydrochloric acid,  $\frac{1}{4}$  lb. of pulverised zinc and 1 oz. of powdered antimony. This gives them a brilliant lustre.

By heating in a bath composed of 1 part tartar emetic, 1 part cream of tartar, 3-4 of hydrochloric acid, and 3-4 of ground antimony, the following tints may be obtained—golden, copper-red, violet, and blue-grey.

A metallic ring can be given to articles made of Britannia metal by heating them in an oil bath to 220°C. and then cautiously raising the temperature to below 3° above the fusing point of the alloy. Small articles must be kept at this temperature for from 15 to 30 minutes, large articles for one hour; the bath is then allowed to cool. The rapidity of the cooling seems to have no appreciable effect (D. Ind. Ztg. 1876, 507); *v.* **ANTIMONY**.

**BRITISH GUM** *v.* **DEXTRINE**.

**BRITTLE SILVER GLANCE** and **BRITTLE SILVER ORES** *v.* **SILVER, ORES OF**.

**BRITTLE SILVER SULPHIDE** *v.* **SILVER, ORES OF**.

**BROCHANTITE**. A native basic copper sulphate found at Roughton Gill, Cumberland, in Arizona, New South Wales, and other places. Made artificially by Meunier (C. R. 86, 686), by allowing fragments of galena to remain for eleven months in a solution of copper sulphate.

**BROGGERITE**. A mineral from Anneröd near Moss, Norway, of sp.gr. 8.73, hardness 5-6. It contains 90.87 U<sub>3</sub>O<sub>8</sub>, 0.81 SiO<sub>2</sub>, 8.41 PbO, 5.64 ThO, 0.38 CeO, 2.42 YO, 1.26 FeO, 0.30 CaO, 0.83 H<sub>2</sub>O (Blomstrand, J. pr. [2] 29, 191; C. J. [2] 46, 1,102).

**BROGNIARDITE**. A sulphantimonite of lead and silver, 2PbAgS.Sb<sub>2</sub>S<sub>3</sub>, from Mexico, containing according to Damour (Ann. Min. [4] 16, 227) 19.38 p.e. S, 29.95 Sb, 25.03 Ag, 24.74 Pb, 0.54 Cu, and 0.04 Zn.

**BROMINE**. Sym. Br. At. wt. 79.75. An element belonging to the class of the halogens; discovered by Balard in 1826. Name from *βρῶμος*, a stench. Never found free; chiefly in combination with alkalis and alkaline earths. As AgBr, in Mexico and Chili; in some Silesian zinc ores, and in Chili saltpetre. In sea-water (in the ratio of 340 mgm. Br to 100 gr. Cl) and in many marine plants and animals, and in many saline springs.

At ordinary temperatures is a dark brown-red liquid of most irritating smell, very volatile; vapour yellowish red, and becoming less transparent when heated.

Boils at 59° and solidifies at -7° to a grey-brown crystalline mass with semi-metallic lustre. Vapour acts on mucous membrane and occasions great irritation. Sp.gr. of liquid 3.18828  $\frac{a}{4}$  (Thorpe). Water dissolves about 3  $\frac{1}{2}$  p.e. of bromine at ordinary temperatures, and the solution when cooled deposits *bromine-hydrate* Br<sub>2</sub>10H<sub>2</sub>O in red octahedral crystals. The solution is of frequent use in analysis as an oxidising agent. Very soluble in alcohol, ether, carbon bisulphide, and chloroform. Acts as a bleacher and disinfectant. A convenient way of using it as a disinfectant is to saturate compressed rods of kieselguhr mixed with 1 p.e. of lime or alkali with the liquid (*v. infra*).

**Extraction and manufacture**. Bromine occurs in nature principally, and so far as its industrial preparation is concerned exclusively, in the shape of bromides, accompanying in small



quantities the chlorides of sodium, calcium, and magnesium. Its quantity is never large enough to admit of its being prepared directly from the raw material, but where the latter is in the first instance worked for sodium chloride and other salts, the bromide accumulates in the mother-liquors, and can be recovered from these. Thus Balard, in 1826, discovered bromine in the mother-liquors obtained on making common salt from sea-water, and for many years it was prepared from the mother-liquors of the saltworks at Kreuznach, Schönebeck, and other places in Germany. It was also found in 1816 in similar mother-liquors in America, especially those at Natrona and Tarentum, later on at Pittsburg, Syracuse, Pomeroy (Ohio), and in the Kanawha region in West Virginia (Mason City, Parkersville, &c.).

Until about 1860 the little bromine that was used was nearly all for scientific purposes. Then, however, medicine and photography began to demand a greater supply of bromides, and later on the manufacture of coal-tar dyes raised an even more extended demand for bromine. It became now remunerative to recover it in the working up of kelp for iodine, but this yielded only little and impure bromine, and was not long continued. An idea was conceived of recovering it from the water of the Dead Sea, but the project, hardly practicable in itself, was given up when Dr. Franck had shown that an ample supply of bromine could be obtained from the mother-liquors of the Stassfurt potash industry (comp. POTASSIUM CHLORIDE). He commenced his practical operations in 1865, when he manufactured about 15 cwt. of bromine; in 1867 the output had already increased to  $7\frac{1}{2}$  tons, and in 1885 the Stassfurt production of bromine was estimated at 260 tons per annum, the price having gone down from 50 or 60 (sometimes as much as 90) marks per kilogramme to  $2\frac{1}{2}$  marks. This lowering of the price was principally due to the fact that since 1878 the Americans had come into the market with bromine made from the above-named salt-works; their liquors contain so much of it that they are able to sell much below Stassfurt prices, but the difficulty of carriage across the ocean prevents the American bromine from encroaching too much upon the European production. The output in America is stated to be about 120 tons. Adding about 20 tons obtained from the nitrate of soda works and elsewhere, the total annual production of bromine may be estimated at present at 400 tons, but much more would be produced, both at Stassfurt and in America, if there was a demand for it.

We shall here give a description of the processes actually followed at Stassfurt, as these have been improved by the constant endeavours of able chemists, and appear to be superior to those practised elsewhere. The raw material worked at Stassfurt, crude carnallite (v. POTASSIUM CHLORIDE), contains bromine in the shape of magnesium bromide, forming about 1 p.c. of the magnesium chloride present. The magnesium bromide accumulates together with the magnesium chloride in the 'final mother-liquor,' which was formerly run to waste in the majority of works, but which may become one of the most important sources of chlorine compounds

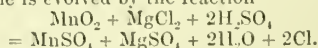
in the world. This mother-liquor contains from 0.15 to 0.35, usually from 0.25 to 0.29 p.c. of bromine. Attempts made to obtain a product richer in bromine by concentration and crystallisation of part of the magnesium chloride have failed, and the liquor is always submitted, as it is, to the process of separating the bromine therefrom.

The separation of the bromine from the solution containing it as magnesium bromide is always effected by means of chlorine. The chlorine is either generated outside and passed into the liquor, or it is generated within the latter by means of hydrochloric acid and manganese ore. A process patented by Leisler in 1865, consisting in distilling the liquor with potassium bichromate and hydrochloric acid, is more costly without offering any corresponding advantage, and seems never to have been practically carried out at Stassfurt.

The apparatus employed by the majority of works (Pfeiffer, H. der Kali Ind. 1887, 323) is shown in fig. 1. A is a chlorine still of about 100 cubic feet in capacity, made in the usual way from heat- and acid-resisting stone, either in one piece or composed of several stones joined in the well-known manner, and strongly bound by iron ties. The stone should be tight without boiling it in tar, as the latter causes losses by combining with bromine, amounting to a hundredweight of bromine for each new coat of tar. *a* is a double bottom consisting of stone flags, on which a charge of 4 cwt. of soft manganese ore is spread, which lasts for several operations. The cover can be lifted up by means of the rope *c*, pulleys *dd*, and counterpoise *e*. It contains a man-hole with lid *f*, an acid-pipe *g*, and a gas-delivery pipe *h*, and a stoneware steam-pipe *k*. *b* is a tank with float for the previous heating of the mother-liquor by means of the steam-coil *l*. Through *l* the spent liquor is run off after each operation into the covered shoot *m*.

The bromine vapour is carried through the lead pipe *n* into the stoneware worm *c*, where liquid bromine is condensed and flows through the glass adapter *u* into the glass bottle *v*, holding 8 litres. The jar *e* serves for receiving the water, condensing together with the bromine and containing chlorine and bromine; it is from time to time syphoned off by *o*. The uncondensed vapours pass into the jar *f*, charged with moist iron borings, where the bromine is retained in the shape of bromide of iron. The jar *f* is so shaped that the liquid, when frothing over its edge, is caught in the annular channel *p* and conducted into the jar *g*.

When the still *a* has received its charge of mother-liquor, previously heated to 60°C. in the tank *b*, the man-hole is closed and 17.5 kilos of sulphuric acid of sp.gr. 1.7 are run in. The acid pipe *g* is closed by a lump of moist clay (this would be unnecessary if it was made to dip below the surface of the liquor within the still), and steam is passed in through *k*, whereupon chlorine is evolved by the reaction



The chlorine at once acts upon the magnesium bromide present and liberates bromine, which passes over at first almost pure, afterwards, when the temperature rises to about 75°C., accom-

panied by water and the chloride of bromine which remains dissolved in the water together with some bromine. If the distillation is carried further, free chlorine is given off as well, and even some hydrochloric acid; it is the latter which at the end of the operation, when acting upon the iron borings in the pan *r*, causes the liquor to froth over in consequence of the evolution of hydrogen. Usually the distillation is only carried on till the pale colour of the gases in the glass adapter *n* shows that there is no more bromine coming over. Each operation generally takes an hour or an hour and a half, and is ended by knocking out the plug *l* and running off the liquor through the covered shoot *m*, which is put in communication with a well-drawing chimney. About once a week the still-cover must be lifted up in order to re-charge the still with manganese. Soft manganese

is preferred to hard, because the dilute acid in *a* does not act well upon the latter.

The bromine condensed in the bottle *v* is run off by a siphon or a glass tap into another stand-bottle holding about 8 litres, and from this into the rectifying apparatus (*v. inf.*). All these operations take place in boxes provided with a strong inward draught in order to protect the men from the bromine vapour.

In the best case each operation yields 2 or 2.5 kilos of bromine, corresponding to a yield of 0.18 to 0.23 p.c. of the mother-liquor; but usually much less, down to 0.1 p.c., is recovered, because it is preferred to avoid the coming over of water and chloride of bromine, which acts very strongly upon the material of the apparatus; also because there is usually an abundance of mother-liquor at disposal. But even in the latter case the usual method entails several

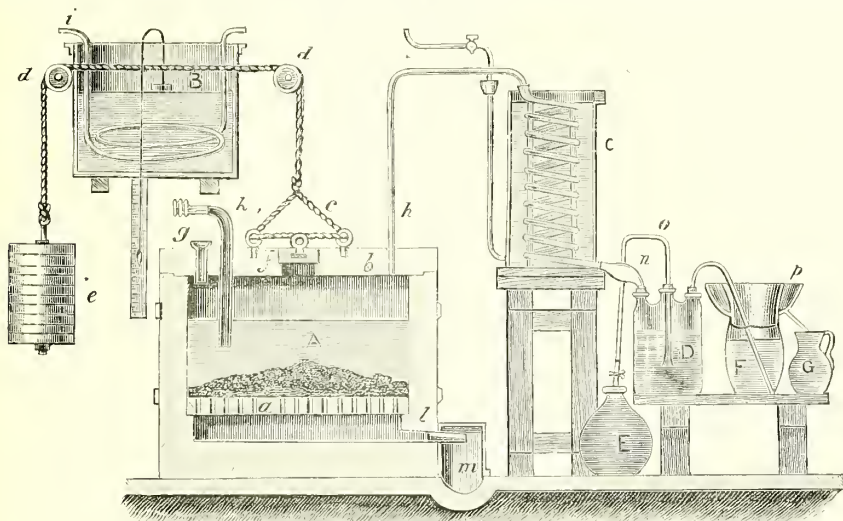


FIG. 1.

drawbacks—namely, losses of time, trouble, and bromine by the constant interruption of work and considerable contamination of the bromine by chlorine. These drawbacks have given rise to the various continuous processes for preparing bromine, the first of which was patented by Dr. Frank in 1878.

In this kind of work the evolution of chlorine always takes place in a separate still, in the usual way, by decomposing manganese ore with hydrochloric acid. The gaseous chlorine is passed successively through a series of decomposing vessels charged with heated mother-liquor, and drives off the bromine, without contaminating it with sulphuric acid and manganese salts and thus disqualifying it from being worked up for solid magnesium chloride, as is the case with the old process. The four decomposing vessels are placed at different levels, so that the mother-liquor run into the top vessel can be made to flow successively through all the four vessels. The chlorine gas enters below the surface of the liquor in the bottom vessel, which is kept at a boiling

heat by means of steam, so that all the bromine still present, together with an excess of chlorine, passes on to the next higher vessel, and so forth to the top vessel. The chloride of bromine formed in the intermediate vessels, when meeting in the top vessel with fresh mother-liquor, yields its chlorine to fresh magnesium bromide, and thus, provided that the current of chlorine has not been too strong, pure bromine vapour will issue at the top end.

This process secures the complete exhaustion of the liquor, together with the complete utilisation of the chlorine and the purification of the bromine from chlorine. Its drawback is not so much the number of connecting pipes and joints as the necessity of introducing the chlorine gas below the surface of the liquor, thus causing a considerable pressure, especially in the chlorine still and in the first decomposing vessel. This drawback is avoided in the apparatus patented in 1882 by the Leopoldshall Chemical Works (G. P. No. 19,780), and shown in the diagram fig. 2. The previously heated mother-liquor flows through the hydraulically-sealed pipe *a*

into the column *A*, constructed of stoneware or of acid-resisting stone. The liquor is here distributed by a perforated pipe *b* and by earthenware balls *cc*, filling the entire space of *A* above the grating. The vapours escaping here pass over by pipe *o* into the worm *p*, cooled by water, and the liquefied bromine is collected in *q*. The cistern *v* contains four stone flags *ss*, leaving an open passage at alternate ends, as shown by the arrows; they are also perforated by a number of small holes. A stone tube *g* serves for introducing steam; it continues at the bottom of *B* in a horizontal tube perforated with a number of holes. The liquor which has passed through the column *A* runs off by tube *z*, flows over the flags *ss* from one to another, and finally issues

by the pipe *i*, leading from the bottom of *B* to the drain *k*, so that *B* is always full of liquor. The contents of *B* being kept boiling by steam-pipe *g*, the steam rises principally through the holes of the flags *ss*, and compels the liquor to flow through the passages left at the alternate sides. Thus the liquor is completely freed from dissolved chlorine and bromine, which rise to the top, where they meet fresh chlorine gas arriving through the pipe *l* (shown in dotted lines) from the washing-cistern *D*. The mixed vapours and steam are conducted through pipe *z*, which is wide enough to admit of their passage, together with that of the liquor flowing in an opposite direction, and in rising up in the column *A* they decompose the magnesium bromide

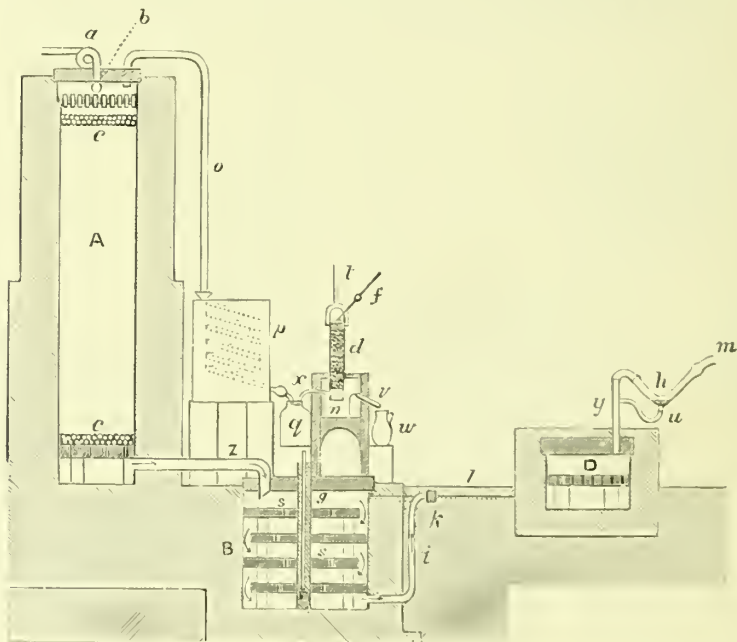


FIG. 2.

contained in the mother-liquor distributed in small drops in the column.

The necessary regularity of the current of chlorine is secured in the following manner. The chlorine gas comes from a still, not shown here, through pipe *m*, to which is joined the bent glass tube *h*, provided with a neck in the angle of its bend. This serves for conducting, by means of an indiarubber tube *u*, the condensed water into the washer *D*. If the free space in the bend does not suffice for the passage of the chlorine, the pressure of the gas will drive some water through *u* into *D*, and thus the level of the liquid in the bend of *h* will sufficiently accurately indicate the rate of evolution of the chlorine. If the current is to be interrupted the elastic tube *u* is taken off from the limb *y*, and the bend of the glass tube *h* is filled with water.

The bromine vapour escaping uncondensed from the bottle *q* passes through *x* into the stoneware tube *d*, suspended in a movable way

by means of rod *t* in the vessel *n*. In the tube *d* there is a grid above the place where tube *x* enters, and another grid is provided near the top, the space between them being filled with iron borings continually kept wet by a stream of water from tube *f*. Thus all the remaining chlorine and bromine is condensed in the shape of iron compounds, the solution containing these overflows through *v* into the jar *w*, while the exhausted air escapes at the top of *d*.

The apparatus just described, by which at present fully half of the bromine manufactured at Stassfurt is produced, completely exhausts the liquor, the yield of bromine being 0.25 p.c. of the mother-liquor—that is, the actual average percentage indicated by analysis. It represents a considerable saving of wages, coals, manganese, and acid in comparison with the old process, and the waste liquor, being practically free from chlorine, causes no nuisance to the neighbourhood.



**Purification of bromine.** Crude bromine contains generally a little chloride of bromine, bromide of lead, and, if it has been in contact with tar, some hydrocarbons. The latter are of high boiling-point, and remain behind on rectifying the bromine, as well as the lead bromide; the chloride of bromine is removed by agitation with a solution of ferrous or potassium bromide, or, as it is more volatile than bromine, by changing the receiver on distillation.

The rectification is carried out in glass retorts, tubulated or not, containing 15 kilos. bromine, and separately placed in sand-baths, consisting of an iron pan reaching to the upper portion of the retort, and heated by a coal fire from below and round the sides. The neck of the retort is connected with a glass adapter, serving for a preliminary cooling, and through this with a receiver in the shape of a narrow necked flask, cooled by being placed in a water tub and by water running on it from the top.

According to Payen, in France they place a little sulphuric acid of sp.gr. 1.80 into the receiver, in order to form a protecting layer over the bromine.

The distillation is carried on by means of a very slow fire, and lasts about twenty-four hours for each operation. Cold draughts are to be carefully avoided in order to prevent the retorts from cracking. When properly treated the latter stand about 10 cwt. of bromine.

The cracking of the retorts is even more easily prevented when heating the sand-baths by means of steam; but the smell of bromine pervading the room is more prevalent in this case. The men have, however, only rarely to enter the room, and protect themselves by tying a wet cloth above the mouths and noses. Men addicted to drinking, or suffering from chest complaints, are much more subjected to the deleterious effects of bromine than others; but in every case they ought to take fatty food (such as bacon, butter, &c.), and to avoid even slight wounds, which heal with great difficulty under the influence of bromine.

Bromine is sold in strong white stoppered bottles, holding one litre, and containing  $2\frac{1}{2}$  or 3 kilos. of bromine; they cost at Stassfurt  $3\frac{1}{2}d.$  each. The glass stoppers must be well ground; they are secured by pouring some shellac on to the joint, covering them with clay putty, and tying wet parement paper over all. Four or six such bottles are placed in a wooden box, the spaces between being tightly filled with sawdust, ashes, or kieselguhr.

Pfeiffer gives the following statement of the cost of producing bromine at Stassfurt with the older kind of apparatus. 1 kilo. of bromine costs:

	Marks
Sulphuric acid, sp.gr. 1.53, 10.8 kilos. } at 44 Pf. . . . .	= 0.475
Manganese ore, 1.04 kilos at 16 Pf. . . . .	= 0.166
Brown coal, 1.15 hectolitres at 40 Pf. . . . .	= 0.460
Wages . . . . .	= 0.193
Packages (bottles, &c.) . . . . .	= 0.208
Repairs . . . . .	= 0.091
Interest and amortisation . . . . .	= 0.100
<b>Total . . . . .</b>	<b>= 1.693</b>

or, say, 1s.  $7\frac{1}{2}d.$

Vol. I.—T

With the continuous apparatus, fig. 2, the cost would be smaller.

The wholesale selling price of the Stassfurt bromine, which is almost chemically pure and quite free from iodine, has been of late 2.5 marks, or temporarily 2.6 to 2.8 marks per kilo.

The principal applications of bromine, whether in the free state or in the shape of bromides, are in photography, in medicine, in the manufacture of a few coal-tar dyes (especially eosine), and in scientific and analytical chemistry; in the latter it has to a great extent taken the place of chlorine, owing to the greater convenience of its manipulation. A similar substitution has been proposed for many technical purposes, but the price of bromine is still too high for this end. It is also a disinfectant, and has found some application for this purpose, especially in the shape of *bromum solidificatum*, patented by Dr. Franck (G. P. No. 21,614). This is kieselguhr, made plastic by means of molasses &c., pressed into sticks of  $\frac{1}{2}$  and  $\frac{1}{4}$  inch diameter, dried, burned to the extent that the sticks acquire a sufficient degree of hardness without losing their porosity, and saturated with liquid bromine in wide-mouthed stoppered glass bottles. After the excess of bromine has been poured off the sticks remain behind, containing about 75 p.c. of the weight of bromine, and are sold in the same bottles. This is a very convenient form of applying it, as a certain number of sticks represents a given weight, and no weighing out of liquid bromine is required; but the retail price of the bromine contained in this *bromum solidificatum* is three or four times as high as the wholesale price of liquid bromine.

**Bromide of iron** is made at Stassfurt, principally for the manufacture of potassium bromide (about 120 tons per annum). It is a compound of the formula  $\text{Fe}_2\text{Br}_6$ , containing 65 to 70 p.c. of bromine, with 0.2 to 0.4 p.c. chlorine (as ferric chloride), 17 p.c. iron, and 12 to 15 p.c. water. We have seen above that in the manufacture of bromine a solution of ferrous bromide ( $\text{FeBr}_2$ ) is obtained; but most of it is made on purpose by passing, in the ordinary distillation process, the first portions of bromine which are free from chlorine into iron borings, contained in a cast-iron or stoneware vessel holding 15 or 20 litres. The solution is passed through a linen cloth or other kind of filter, and is converted into the compound  $\text{Fe}_2\text{Br}_6$  by adding to it more bromine in a cast-iron pan heated to a sufficient temperature. This newly added bromine is required to be free from chlorine, and it can be made so without distillation by agitating it with ferrous bromide solution, which takes up all the chlorine. The brown-red solution of iron bromide is then evaporated to a paste and poured into shallow iron boxes, where it solidifies into a blackish-brown crystalline mass, which is tightly packed in small kegs, and sold according to the quantity of bromine it contains. G. L.

**Hydrobromic acid.**  $\text{HBr}$ . *Bromhydric acid*, *Hydrogen bromide*. A colourless pungent gas of irritating smell; fumes strongly in the air. Condensed to a liquid at  $-73^\circ$ . May be obtained synthetically by passing bromine and hydrogen through a hot tube or over heated platinum. Best prepared by action of phos-

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phorus and bromine on water.  $5\text{Br} + \text{P} + 11\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 5\text{HBr}$ ; or by the action of a concentrated solution of  $\text{H}_3\text{PO}_4$  on  $\text{KBr}$ ; or by dropping  $\text{Br}$  upon melted paraffin heated to  $185^\circ$ .

Gas very soluble in water; solution when saturated forms a colourless strongly acid liquid of sp.gr. 1.78, and contains 82 p.c.  $\text{HBr}$  by weight, corresponding to the formula  $\text{HBr} \cdot 11\text{H}_2\text{O}$ . If the concentrated acid be heated at ordinary pressures the gas is evolved until the amount of  $\text{HBr}$  in the solution sinks to 47 p.c. when the liquid boils constantly at  $126^\circ$  under a pressure of 760 mm. This proportion of  $\text{HBr}$  corresponds to  $\text{HBr} + 5\text{H}_2\text{O}$ , but the liquid is not a true hydrate, since the composition is altered by varying the pressure; thus if the pressure be raised to 1.95 m. the solution boils at  $153^\circ$  and contains 46.3 p.c.  $\text{HBr}$ .

The sp.gr. at  $15^\circ$  and p.c. composition of aqueous solutions of hydrobromic acid is given in the following table (Wright, C. N. 23, 212):

Sp. gr.	HBr p.c.	Sp. gr.	HBr p.c.
1.080	10.4	1.385	40.8
1.190	23.5	1.175	48.5
1.248	30.0	1.515	49.8

For pharmaceutical purposes a dilute solution of hydrobromic acid may be prepared by dissolving  $84\frac{1}{2}$  grains of potassium bromide in a fluid ounce of water and adding 9 grains of tartaric acid to the solution. After standing, acid potassium tartrate crystallises out and the solution contains about 10 p.c. of hydrobromic acid. Hydrobromic acid has been used in the treatment of ear complaints.

**BROMITE.** Native silver bromide found in Mexico and in Chili, *v.* SILVER.

**BROMOFORM** *Tribrommethane*  $\text{CHBr}_3$ . This substance is occasionally met with in the liquid left after the rectification of bromine in which it occurs associated with *chlorobromoform*  $\text{CHBr}_2\text{Cl}$  (Dyson, C. J. 13, 46) and *carbon tetrabromide*  $\text{CBr}_4$  (Hamilton, C. J. 39, 48). It may be made by the simultaneous action of bromine and caustic potash or of bromide of lime on alcohol or acetone, or by the action of alkalis on bromal. It is, when pure, a colourless liquid solidifying at  $8^\circ$  and boiling with slight decomposition under ordinary pressure at  $151^\circ$ . Sp.gr.  $2.902$   $^{15^\circ}$  (Perkin, C. J. 45, 533). It has been used to a slight extent as an anæsthetic, and in the treatment of diphtheria.

**BRONZE** *v.* TIN.

**BROOKITE** *v.* TITANIUM, OCCURRENCE OF.

**BROOM, DYERS', or GREENWEED.** The *Genista tinctoria*, a dwarf shrub from the flowers of which a bright yellow colour is obtained, which for dyeing green with woad is said to be preferred by dyers to all other yellows. *Genista pilosa*, from the Ardennes, contains 2.54 p.c. of nitrogen and 2.91 p.c. of ash, composed of 43.28 p.c.  $\text{K}_2\text{O}$ , 4.18  $\text{Na}_2\text{O}$ , 18.57  $\text{CaO}$ , 10.05  $\text{MgO}$ , 1.12  $\text{Fe}_2\text{O}_3$ , 4.61  $\text{SO}_3$ , 14.05  $\text{P}_2\text{O}_5$ , 1.11  $\text{SiO}_2$ , 3.89  $\text{Cl}$ , and is therefore a useful manure (Petermann, A. A. 9, 251).

**BROOM TOPS.** *Scoparinus*. (*Genêt à balais*, Fr.; *Besenginster*, Ger.) The tops of the common broom, *Cytisus scoparinus* (Link, B. a. T. 70), have been employed for their diuretic and purgative properties since the Anglo-Saxon period, and are noticed in nearly all the herbals

and pharmacopæias. The older writers describe the broom under the name 'genista,' 'genesta,' or 'genestra,' and it was the wearing of the 'planta genista' as an emblem by Geoffrey, Count of Anjou, that gave the title 'Plantagenet' to his royal descendants (Comp. Fl. a. H. 170).

Stenhouse in 1851 discovered in broom-tops a liquid alkaloid *sparteine*,  $\text{C}_{15}\text{H}_{25}\text{N}_3$ , together with a chemically indifferent crystallisable compound *scoparin*  $\text{C}_{21}\text{H}_{33}\text{O}_{10}$  (A. 78, 15). *Sparteine* has been further investigated by Mills (C. J. 15, 1), Houde (J. Ph. [5] 13, 39), Bamberger (A. 235, 368), Coninek (C. R. 101, 513), and Ahrens (B. 20, 2218; 21, 825). To obtain it Mills distils the tops with soda, separates the crude oil which comes over, acidifies it, and redistils with soda. The impure alkaloid is then dried in a current of hydrogen, the adhering soda removed, and finally it is submitted to fractional distillation. It is a viscid, colourless oil, with an unpleasant odour and bitter taste. It sinks in water, in which it is nearly insoluble. B.p.  $288^\circ$  (Stenhouse; *cf.* Bamberger; Bernheimer, G. 13, 151). With acids *sparteine* combines, forming crystallisable salts.— $\text{B}'(\text{HCl}) \cdot \text{PtCl}_2 \cdot 2\text{Ag}$ , yellow crystalline powder (Mills).— $\text{B}'(\text{HCl})_2 \cdot \text{AuCl}_3$  (Mills).— $\text{B}''\text{H}_2\text{SO}_4$ , large prisms, *v.* sol. water (Bamberger).— $\text{B}'''$ , four-sided plates, sol. hot water (Bamberger);  $\text{B}''(\text{HCl})_2$ , silky needles (Bamberger). *Sparteine* is a narcotic poison resembling nicotine, but less active (Stenhouse, *cf.* Sée, C. R. 101, 1016). A characteristic orange-colour reaction is said to be produced when *sparteine* or its salts are added to sulphurate of ammonium (Grandval a. Valser, J. Ph. [5] 11, 65).

The more important reactions of *sparteine* are:—1. Nitric acid converts it into a compound which yields chloropierin when treated with chloride of lime (Stenhouse).—2. Oxidised with potassium permanganate it yields formic and oxalic acids (Bamberger; Ahrens).—3. Oxidised by peroxide of hydrogen a new base  $\text{C}_{15}\text{H}_{25}\text{N}_3\text{O}_2$  is formed. It is syrupy, colourless, not crystallisable, and distils with difficulty with steam. Platinum salt,  $\text{B}''(\text{HCl}) \cdot \text{PtCl}_4$ , blackens at  $235^\circ$ , and gold salt  $\text{B}'(\text{HCl}) \cdot \text{AuCl}_3$  melts at  $113.6^\circ$  (Ahrens).—4. Reduced by nascent hydrogen a colourless oil, *dihydrosparteine*  $\text{C}_{15}\text{H}_{25}\text{N}_2$ , results. It boils at  $281.4^\circ$ , and forms a crystalline platinum salt  $\text{B}''(\text{HCl}) \cdot \text{PtCl}_4$ , which blackens at  $239^\circ$  (Ahrens).—5. With alkyl iodides and alcohol *sparteine* reacts, forming  $(\text{C}_3\text{H}_7\text{EtN})_3\text{I}$  (Mills) and  $(\text{C}_3\text{H}_7\text{MeN})_2\text{I}$  (Coninek), which compounds by the action of oxide of silver yield the hydride  $(\text{C}_3\text{H}_7\text{EtN}_2)(\text{OH})_2$  (Mills) and by the action of soda  $(\text{C}_3\text{H}_7\text{EtN}_2)\text{EtI}$  and  $(\text{C}_3\text{H}_7\text{MeN}_2)\text{MeI}$  (Bamberger). Mills also obtained a diethyl di-iodide  $(\text{C}_3\text{H}_7\text{EtN}_2)_2\text{I}_2$ .—6. Heated with concentrated hydriodic acid at  $200^\circ$ , methyl in the form of methyl iodide is removed, and there remains a new base  $\text{C}_{15}\text{H}_{25}\text{N}_2$ . B.p.  $276^\circ$  (Ahrens).—7. When *sparteine* is distilled with lime the distillate contains ethylene, propylene, (*γ*) picoline, and a new tertiary base (Ahrens).

Scoparin is obtained from broom-tops, after a series of processes to free it from the chlorophyll with which it is associated, as a pale yellow powder which may with difficulty be made to crystallise. It is sparingly soluble in water, but is soluble in alcohol and alkalis. Its

solution in ammonia is deep yellow-green. With chloride of lime a green colour is produced. Nitric acid converts it into picric acid. Melted with potash it gives phloroglucin and proto-catechuic acid (Hlasiwetz, A. 138, 190). Heated with alcohol a less soluble modification, *isoscoparin*, is formed, which is readily reconverted into scoparin by solution in alkali and precipitation by an acid (Stenhouse). A. S.

**BROSIMUM UTILE.** The latex of this urticaceous tree, growing in Venezuela, approximates to cow's milk in composition. It contains 35·2 p.c. of wax and saponifiable matters which are used in the manufacture of candles (Boussingault, Ph. [3] 9, 679).

**BROUSSONETIA PAPYRIFERA.** *The paper mulberry.* The fibrous bark is used in China and Japan for the manufacture of a kind of paper, and in Polynesia in the manufacture of *Tapa* cloth.

**BROUSSONETIA TINCTORIA** v. YELLOW WOOD.

**BROWN, ACID,** v. AZO-COLOURING MATTERS.  
**BROWN, ANILINE,** v. BISMARCK BROWN.  
**MANCHESTER BROWN,** PHENYLENE  
**BROWN, VESUVINE, LEATHER BROWN,**  
**CINNAMON BROWN, ENGLISH BROWN,** or  
**GOLD BROWN;** v. AZO-COLOURING MATTERS.

**BROWN, ANTWERP,** v. PIGMENTS.  
**BROWN, ARCHIL,** v. AZO-COLOURING MATTERS.

**BROWN, BISMARCK,** v. AZO-COLOURING MATTERS.

**BROWN, BONE,** v. PIGMENTS.  
**BROWN, CALEDONIAN,** v. PIGMENTS.  
**BROWN, CAPHEK,** v. PIGMENTS.  
**BROWN, CINNAMON.** *Aniline brown* v. AZO-COLOURING MATTERS.

**BROWN, ENGLISH.** *Aniline brown* v. AZO-COLOURING MATTERS.

**BROWN, FAST,** v. AZO-COLOURING MATTERS.  
**BROWN, GARNET.** The potassium or ammonium salt of isopurpuric acid ( $C_{12}H_5N_2O_6K$  or  $C_{12}H_5N_2O_6$ ). Obtained by Hlasiwetz in 1859 by the action of potassium cyanide on picric acid (A. 110, 289). Forms a dark-brown powder, readily sol. in hot water with reddish-brown colour. Dyes wool and silk brown in an acid bath. No longer in use. (V. also ISOPURPURIC ACID.)

**BROWN, GOLD.** *Aniline brown* v. AZO-COLOURING MATTERS.

**BROWN, LEATHER.** *Aniline brown* v. AZO-COLOURING MATTERS.

**BROWN, MADDER,** v. PIGMENTS.  
**BROWN, MANCHESTER,** v. AZO-COLOURING MATTERS.

**BROWN, NAPHTHYLAMINE,** v. AZO-COLOURING MATTERS.

**BROWN, PHENYL,** v. PHENYL BROWN.  
**BROWN, PHENYLENE,** v. AZO-COLOURING MATTERS.

**BROWN, PICRYL,** v. PICRYL BROWN.  
**BROWN, PIGMENT,** v. AZO-COLOURING MATTERS.

**BROWN, PRUSSIAN,** v. PIGMENTS.  
**BROWN, RESORCIN,** v. AZO-COLOURING MATTERS.

**BROWN, SOUDAN,** v. AZO-COLOURING MATTERS.

**BROWN, VANDYKE,** v. PIGMENTS.

**BROWN, VERONA,** v. PIGMENTS.

**BROWN BERRIES.** The fruit of *Rubus fruticosus*.

**BROWN COAL** v. FUEL.

**BROWN HÆMATITE** v. IRON, ORES OF.

**BROWN IRON ORE** (*Limonite*) v. IRON, ORES OF.

**BROWN OCHRE.** A soft variety of brown iron ore occasionally used as a pigment.

**BRUCINE** v. VEGETO-ALKALOIDS.

**BRUCITE.** Native hydrate of magnesia. That found at Cogne, Val d'Aosta, contains, according to Friedel (Gazzetta, 13, 278; J. C. S. 46, 162), 68·53 MgO, 1·15 FeO, and 30·13 H<sub>2</sub>O.

**BRUNSWICK BLACK.** Is prepared by fusing 2 lbs. of asphalt, and mixing thoroughly with 1 pint of hot boiled oil. When cool, 2 pints of turpentine are added to the mixture. An inferior but cheaper black may be made by boiling gently together for five hours 25 lbs. each of black pitch and gas tar asphaltum; 8 gallons of linseed oil, and 10 lbs. each of litharge and red lead, are then mixed in, and the whole boiled. After cooling, the mixture is thinned by the addition of 20 gallons of turpentine. V. also BONE OIL.

**BRUNSWICK GREEN.** An oxychloride of copper, used as a pigment. Copper filings or turnings are moistened with a solution of sal-ammoniac, and left in contact with the air; the oxychloride so formed is washed off with water, and dried at a gentle heat. The term is also applied to chrome green, and to emerald green (v. COPPER AND PIGMENTS).

**BRUSHITE.** A hydrated phosphate of lime occurring in the guano of Aves Island and Sombbrero in the Caribbean Sea.

**BRYOIDIN** v. OLEO-RESINS.

**BUBULIN** (from *Boés*, ox). The name of a peculiar substance said by Morin to exist in cow-dung, and to be copiously precipitated by metallic salts, tincture of galls, and alum, and therefore to be active in the application of cow-dung to calico-printing.

**BUCHU.** The leaves of three varieties of *Barosma* (order Rutaceæ), viz. *B. betulina*, *B. crenulata*, and *B. serratifolia*, are known under this name. Brandes (Arch. d. N. Apoth. Ver. 22, 229) found in 1,000 parts, 88 parts volatile oil and 40 parts of a yellowish-brown bitter substance, soluble in water, which he called *diosmin*. Landerer (Buchner's Répert. 84, 63) found in the alcoholic tincture a crystalline deposit insoluble in water. Flückiger (Ph. 3, 4, 689) obtained from the essential oil a camphor melting at 85° and subliming at 110°, and having the constitution  $C_{10}H_{16}O$ . Wayne (Ph. 3, 6, 723) obtained salicylic acid from the oil after treating with strong soda solution; in other experiments he obtained a crystalline body probably identical with the diosphenol isolated by Flückiger by an analogous treatment (Ph. [3] 11, 219). Diosphenol has the composition  $C_{11}H_{12}O_3$ ; it forms large prisms, melting at 83° and boiling at 233°. In addition to this body, Flückiger (*l.c.*) has found in the oil a substance boiling 205°-210° C., possessing an odour very like that of peppermint; its composition is  $C_{10}H_{14}O$ .



**BUCKTHORN** (*Rhamnus catharticus*). This plant is a native of England; it grows to the height of from 15 to 20 feet; its flowers are greenish-coloured and its berries four-seeded. It is the fruit of this plant which is sold as a purgative under the name of French berries. The juice of these, when in an unripe state, has the colour of saffron; when ripe and mixed with alum, it forms the sap or bladder green of the painters; and in a very ripe state the berries afford a purple colour. The bark also yields a fine yellow dye, rhamnoxanthin; *v.* SARGREEN; PIGMENTS.

The alder buckthorn (*Rhamnus Frangula*) grows naturally, and is very abundant in woods and thickets in some parts of Britain. The berries of this species are often substituted for those of the above; but they are easily detected, since they contain only two seeds. In a green state, they dye wool green and yellow; when ripe, bluish-grey, blue, and green. The bark also dyes yellow, and, with preparation of iron, black (Lawson); *v.* *Frangulin*, art. GLUCOSIDES.

**Rock buckthorn** (*Rhamnus saxatilis*), the berries of which are used to dye morocco leather yellow. These, in common with the narrow-leaved buckthorn berries (*R. Chusii*) and those of the yellow-berried buckthorn (*R. infectorius*), are sold as Avignon berries. The wood of the *Rhamnus erythroxylon* (which is a native of Siberia, but grows freely in this climate), in a ground state yields the bright red colour known to dyers under the name of *redwood*. These possess violent purgative properties due apparently to *rhamnegin*.

**BUCKWHEAT.** (*Blé Sarrasin*, Fr.; *Buckweizen*, Ger.) The common buckwheat (*Polygonum Fagopyrum*) is cultivated for feeding pheasants and other game; and is now being largely used in France and in this country in distilleries.

In France, besides being used for feeding fowls, pigs, &c., it is given to horses; and it is said that a bushel of its grains goes further than two bushels of oats, and if mixed with four times its bulk of bran, will be full feeding for any horse for a week. Its haulm, or straw, is said to be more nourishing than that of clover, and its beautiful pink or reddish blossoms form a rich repast for bees (Lawson).

It has been stated that the leaves of the common buckwheat (*Polygonum Fagopyrum*) yield, by fermentation, indigo-blue. On examining this plant, for the purpose of ascertaining whether this statement was correct, Schunck was unable to obtain a trace of that colouring matter; but he discovered that the plant contains a considerable quantity of a yellow colouring matter, which may very easily be obtained from it. This colouring matter crystallises in small primrose-yellow needles. It is very little soluble in cold water, but is soluble in boiling water, and still more soluble in alcohol. Muriotic and sulphuric acids change its colour to a deep orange, the colour disappearing on the addition of a large quantity of water. It dissolves easily in caustic alkalis, forming solutions of a beautiful deep yellow colour, from which it is again deposited in crystalline needles on adding an excess of acid. It is, however, decomposed when its solution in alkali is exposed for some time to the air, being

thereby converted into a yellowish-brown amorphous substance resembling gum. Its compound with oxide of lead has a bright yellow colour, similar to that of chromate of lead. The compounds with the oxides of tin are of a pale but bright yellow colour. On adding ferrous sulphate to the watery solution, the latter becomes greenish, and, on exposure to the air, acquires a dark-green colour, and appears almost opaque. The watery solution imparts to printed calico, colours, some of which exhibit considerable liveliness. Silk and wool do not, however, acquire any colour when immersed in the boiling watery solution, unless they have previously been prepared with some mordant. Its formula is probably  $C_{15}H_{12}O_{10}$ . It appears to be identical with *rutine*, the yellow colouring matter contained in the *Ruta graveolens*, or common rue, and in capers, and with *Nixanthin*, a substance derived from the leaves of the common holly. From 1,000 parts of fresh buckwheat leaves, a little more than 1 part of the colouring matter may be obtained. As the seed of the plant is the only part at present employed, it might be of advantage to collect and dry the leaves, to be used as a dyeing material (Schunck).

The Tartarian buckwheat (*Polygonum tataricum*) differs from the former in having the edges of its seeds twisted. It is not considered so productive, but it is more hardy and better adapted for growing in mountainous situations.

The **dyer's buckwheat** (*Polygonum tinctorium*). This plant was introduced to the royal gardens at Kew by Mr. John Blake, in 1776. Authentic information as to its properties as a dye-yielding plant was only received at a comparatively recent period, from missionaries resident in China, where it has always been cultivated for its colouring matter. In Europe attention was first directed to its growth by M. Delille, of the Jardin du Roi at Montpellier. The Japanese are said to extract blue dyes from *Polygonum Chinese*, *P. barbatum*, and the common roadside weed *P. aviculare* (Lawson).

**BUCURUMANGA RESIN.** A fossil resin occurring in an auriferous alluvium near Buecurumanga, New Granada. It is light-yellow, transparent, somewhat heavier than water, becomes strongly electric by friction; is insoluble in alcohol; swells up in ether, becoming opaque; melts when heated; burns in the air without residue. It resembles amber in outward appearance, but does not give succinic acid on dry distillation. It contains 82.7 p.c. C, 10.8 H, and 6.50 O (Boussingault, A. Ch. [3] 6, 507); *v.* RESINS.

**BUFFALO RUBIN** *v.* AZO-COLOURING MATTERS. **BUNTUPFERERZ** (Ger.) Variegated copper ore. This term is commonly applied, even by English mineralogists, to an ore of copper otherwise known as *Bornite* (*q.v.*), *Erbescite*, *Phillipsite*, and *Purple Copper Ore*. Called 'horse-flesh ore' by the Cornish miners (Urc).

**BURGUNDY PITCH, or NORWAY SPRUCE RESIN.** (*Fichtlenarr*, *Tannenhardt*, Ger.; *Poix des Vosges*, *Poix blanche*, *Poix jaune*, *Barras*, Fr.) The resin of *Abies excelsa* purified by melting in hot water and straining. It is an opaque, yellowish-brown, hard, brittle resin; its taste is sweet and aromatic. It is very soluble in glacial acetic acid, acetone, and alcohol. Used in

making plasters. It is much adulterated. The substance usually sold by this name in England is made by melting colophony with palm-oil or some other fat, and stirring in water to make the mixture opaque (Morel, Ph. [3] 8, 342); *v. RESINS*.

**BURNETT'S FLUID.** A solution of zinc chloride is commonly known as Sir William Burnett's disinfecting fluid. It is largely used as a disinfectant.

**BURTON WATER CRYSTALS** contain, according to Moritz a. Hartley, 31.8 CaO, 40.4 SO<sub>3</sub>, 1.04 Cl, 5.46 MgO, and 21.19 OH<sub>2</sub> (S. C. I. 2, 82).

**BUSSORAH GUM v. GUMS.**

**BUTEA GUM.** The juice of *Butea frondosa* (Roxb.), often sent into the market instead of genuine kino. It forms black-brown, slightly lustrous, brittle lumps, has an astringent taste, and yields pyrocatechin by dry distillation.

**BUTTER.** The fatty constituent of milk, and chiefly that derived from the milk of the cow. The fat exists in the state of minute globules suspended in the milk liquid, and when the milk is left at rest the globules rise to the top, forming a layer of cream, which contains considerable proportions of casein and milk fluid. The particles of fat are surrounded by a film of casein or condensed fluid resulting from local attraction. Butter is obtained from cream by agitation or churning, which causes the fat globules to aggregate in the milk fluid.

*Description.*—Common butter is more or less granular, and varies in colour from almost white to deep yellow. It contains variable proportions of curd and water, the former ranging from .2 to upwards of 4 p.c., and the latter from 4 to 18 p.c. The curd is liable to undergo decomposition and to cause the butter to become rancid through the separation of the soluble acids. When freed from curd, butter fat possesses considerable permanence of character, and may be kept for a long time without any appreciable change. The curd and water may be separated by melting the butter in a suitable vessel, when the butter fat, which rises to the top, can be drawn off from the curd and water, which remain at the bottom. Butter is composed of fatty acids in combination with glycerine, forming compound ethers of a complex constitution. The fatty acids found in butter are butyric, caproic, caprylic, capric, myristic, palmitic, stearic and oleic acids. The first four, which are more or less soluble in hot water, are described as soluble, and the remaining four, which are insoluble in boiling water, are called insoluble. According to a proximate analysis by Bell, butter contains 6.13 p.c. butyric acid, 2.09 caproic, caprylic, and capric acids, 49.46 palmitic, stearic, and myristic acids, and 36.10 oleic acid. According to the same authority, the molecule of butter fat does not necessarily contain three radicles of the same acid, but three different acid radicles forming a tri-acid compound (Chemistry of Foods, 2, 44-50).

*Analysis.*—The analysis of butter may be divided into three parts. 1. The estimation of the water, salt, curd, and fat; 2. the determination of the specific gravity of the fat; and 3. the estimation of the soluble and insoluble fatty acids. The water is determined by drying a

weighed quantity of the butter at 100°; the salt and curd by extracting the fat from the dried butter with ether or petroleum spirit, the salt being afterwards dissolved by water and the chloride determined by precipitation or titration. The sp.gr. of the dry filtered fat is taken at 37.7°. The fat is poured into the bottle several degrees above the standard temperature, to which point it is gradually brought down when the bottle is quickly filled from the residue of fat cooled to 37.7° (Bell, Parliamentary Paper, No. 293, 1876). A modification of this method for facilitating the determination of the sp.gr. has been proposed by Estcourt (C. N. 34, 254). Fats should not be maintained at a high temperature for any length of time before taking the sp.gr., as an increase takes place in the density in consequence of oxidation.

The co-efficient of expansion of butter is .0434 for each degree F. from 100-212 (C. J. 1880, 70).

The soluble and insoluble fatty acids are estimated by saponifying a weighed quantity of dry butter fat with solution of soda of indefinite or of known strength, according to whether the insoluble acids or the acids of both kinds are to be determined. In the latter case two solutions are prepared—a normal alcoholic solution of soda, and a solution of H<sub>2</sub>SO<sub>4</sub> slightly stronger than the soda solution. 25 c.c. of the former are added to 4 or 5 grams of dry butter fat in an assay flask and saponified. The soap, while hot, is decomposed by 25 c.c. of H<sub>2</sub>SO<sub>4</sub> solution; the insoluble acids are separated by filtration, dried and weighed, and the filtrate is titrated with decinormal soda solution. The number of c.c. required, less the number of c.c. by which the H<sub>2</sub>SO<sub>4</sub> solution exceeds the soda solution, represents the soluble acids derived from the butter.

The suggestion for the estimation of the insoluble acids was made by Hohner and Angel (Pamphlet, July 1874), and that of the soluble acids by Dupré (Analyst, June 1876). A method for the separation of the insoluble acids in the cold has been proposed by Muter (Analyst, 1876, p. 7). The use of paraffin for facilitating the separation of the insoluble acids has been suggested by Hager (C. J. 1879, 2, 81). Reichart has recommended several modifications of the process for determining the soluble and insoluble acids. The former he separates by distillation before titration (C. J. 1879, 2, 406). Perkins has likewise proposed the distillation of the soluble acids before titration, and subsequent titration of fixed acids (C. J. 1879, 2, 1,070). A process for estimating both kinds of acids, based upon the difference between the solubility of their barium salts, has been described by Knight (C. J. 1881, 2, 201). Koettstorfer has recommended a method, founded on molecular data, for testing butter by titration of the total acids (C. J. 1879, 2, 983); but Wigner has pointed out defects in the system (C. J. 1880, 2, 69). Heintz considers that the presence of the insoluble acids does not affect the accurate titration of the soluble acids (C. J. 1878, 78). Meissl, after saponification, distills with H<sub>2</sub>SO<sub>4</sub> and titrates the distillate (C. J. 1880, 2, 828).

*Adulteration.*—When butter fat is adulterated it is usually with an excess of water or salt, or

an admixture of ordinary animal or vegetable fats. In commercial butters the water has been found to vary from 4 to about 18 p.c. In genuine butters the insoluble fatty acids have been found to vary from 85.56 to 89.90, and the soluble from 4.50 to 7.41 p.c. (Chemistry of Foods by Bell, Part II. 64). This range has been confirmed by Fleischmann and Veith (C. J. 1879, 181); Jahre (C. J. 1873, 685) and others.

In ordinary animal fats the insoluble fatty acids vary from 95.56 to 96.20 p.c., and they differ furthermore from butter in not containing any of the soluble fatty acids.

The sp.gr. of butter fat at a temperature of 37.7° also differs materially from that of ordinary animal fats at the like temperature. Thus the sp.gr. of butter fat varies from 909.37 to 913.91 (the ordinary range being 911 to 913) while that of ordinary animal fats ranges from 902.83 to 903.84. These several differences become available for testing the purity of a butter and also for estimating the proportion of foreign fat, if any,

present. The estimation of the fatty acids is somewhat tedious and difficult of execution, but the determination of the sp.gr. of the fat, which is a comparatively easy operation, is sufficient to show whether the butter is pure or not. The correspondence between the sp.gr. of the fats and the percentage of fixed fatty acids is sufficiently close to admit of the predication of either from the other within a few tenths, the sp.gr. of butter fat increasing regularly as the proportion of fixed fatty acids diminishes.

According to Warren (C. N. 222, 1887), when a solution of butter fat in carbon disulphide is treated with yellow sulphur chloride, and the disulphide is evaporated over hot water, the resulting thickened mass should yield a clear solution with carbon disulphide. An insoluble or dark residue will indicate the presence of a vegetable oil.

The ten samples in the following table represent the ordinary variations in the composition of butter fat:—

Percentage					Butter Fat			
No.	Water	Salt	Curd	Butter Fat	Specific Grav. at 100°F.	Per Cent. Fixed Acids	Per Cent. Soluble Acids as Butyric Acid	Melting Point Fahr.
1	7.55	1.03	1.15	90.27	913.89	85.56	7.41	85
2	11.71	3.60	.95	83.74	911.45	88.24	5.41	90
3	16.89	8.56	1.23	73.32	911.48	88.82	4.64	89.5
4	16.28	3.32	1.56	78.84	912.79	86.00	7.00	88.5
5	11.42	1.29	1.12	86.17	910.47	88.53	4.84	90
6	12.55	.89	.74	85.82	910.20	89.00	4.57	90
7	12.96	2.43	1.25	83.36	912.51	88.25	5.45	89
8	13.40	1.39	2.03	83.18	911.67	88.72	5.07	90
9	12.05	.96	1.95	85.04	911.04	87.51	5.28	88
10	14.62	1.48	1.88	82.04	910.70	89.00	4.50	91

The following table shows the sp.gr. of ordinary animal fats at 100 F. (37.7°C.), and also the percentage of fixed fatty acids contained in each:—

Description	Specific Gravity at 100°F.	Percentage of fixed Fatty Acids
Mutton suet . . .	902.83	95.56
Beef suet . . .	903.72	95.91
Fine lard . . .	903.84	96.20
Dripping (commercial) .	904.56	94.67
Mutton dripping (genuine)	903.97	95.48

J. B.

**BUTTER BEANS.** The dried seeds of *Vateria indica*, a tree growing in India, especially in Malabar. They contain 49.21 p.c. of a greenish-yellow solid fat, resembling mutton tallow in hardness and viscosity. It consists of 81 p.c. neutral fatty glycerides and triolein and 19 p.c. free fatty acids. The fatty acids obtained on saponifying melt at 56.6 (Höhnle, Wolfbauer; D. P. J. 252, 333; J. C. S. 2146, 1209).

**BUTTERS, MINERAL.** A term formerly applied to several of the metallic chlorides, e.g. chlorides of antimony, tin, bismuth, zinc, &c.

**BUTTERINE** v. **MARGARINE.**

**BUTTER YELLOW.** *Aniline-azo-dimethyl aniline*  $C_6H_5N : N.C_6H_4(CH_3)_2$ . A yellow colouring matter (m.p. 115°); insoluble in water, soluble in dilute HCl, with red colour. Soluble in fats. Used for colouring butter (Witt. Griess. B. [1877] 10, 528).

**BUTTER SURROGATE** v. **MARGARINE.**

**BUTTER VEGETABLE.** A greasy substance expressed from the kernel of the *Bassia butyragracea*, a native of North India. This grease is said to make excellent soap. Shea butter is obtained from the *B. Parkii*, of West Africa, and has been used in making candles and soap. The butter-tree of Sierra Leone is the *Pentadesma butyragracea* (Br.), the fruit of which yields much grease, eaten by the negroes.

**BUTYRIC ACID**  $DC_4H_9O_2$ . Two isomeric forms of this acid are known, normal butyric and isobutyric acid.

**Normal butyric acid**  $CH_3CH_2CH_2COOH$ .

**Occurrence.** In ordinary butter in combination with glycerine to the extent of 2 p.c.; also in the fruits of *Heracleum giganteum* and of *Pastinaca sativa*, as hexyl butyrate and octyl butyrate respectively. Butyric acid is also found in flesh juice, and is frequently a constituent of decomposing organic matter (J. 1857, 353, 402, 403, 559; 1858, 231; 1859, 363, 364; 1861, 454; 1866, 311).



*Preparation.*—(1) Butyric acid is a frequent product of the oxidation of organic substances; casein, fibrin and albumen, for example, yield this acid among other products on oxidation with manganese dioxide and sulphuric acid (Guckellberger, A. 64, 68).

(2) All amylaceous and saccharine substances which yield lactic acid as a product of their fermentation can undergo a further fermentation to butyric acid, and this fact is made use of for the preparation of the acid. 5 kilos. of rice or potato starch are boiled with 60 litres of water for some hours, allowed to cool, and the product after 24 hours is treated with 60 grams of malt stirred up with 2 litres of milk, with 1 kilo. of finely-divided flesh, and with 2 kilos. of chalk, the chalk being added to neutralise the lactic and butyric acids as rapidly as they are formed, and the whole is allowed to remain with occasional stirring for several weeks at a temperature of 25°–30°. When the evolution of gas has ceased, the product is heated to 80°, filtered, precipitated with sodium carbonate to decompose the calcium salt, again filtered, evaporated to a small bulk, and treated with sulphuric acid. The oily layer of acid so obtained is fractionated to free it from the acetic and caproic acids formed simultaneously, and the fraction 155°–174° is extracted with water, which dissolves the butyric acid but leaves the caproic acid undissolved; the aqueous extract is then neutralised with lime, the solution concentrated, and the salt finally decomposed by hydrochloric acid (Grillone, A. 165, 127).

(3) In the presence of a schizomyces—the so-called *Bacillus subtilis*, which can readily be obtained by stirring hay in water, straining the liquor through a sieve, and boiling for 5 minutes—Fitz (B. 11, 52) has found that starch readily undergoes fermentation yielding normal butyric acid as chief product. Nitrogenous materials and phosphates must be present for the growth of the organism. In one experiment 100 grams of potato starch were mixed with 0.1 gram of potassium phosphate, 1 gram of ammonium chloride, 0.02 gram of magnesium sulphate, 50 grams of chalk, and 2 litres of water at 40°, and the mixture, treated with a small quantity of the liquid containing the bacillus, yielded after 10 days' standing 31.7 grams of butyric acid, together with 1 gram of ethyl alcohol, 5.1 grams of acetic acid, and 0.33 gram of succinic acid. It is to be supposed, however, that just as it is now possible by the use of a pure lactic ferment to obtain pure lactic acid without the fermentation tending to proceed further by conversion of the acid so formed into butyric acid, so, by obtaining pure cultivations of the particular bacterium which effects the change of lactic acid into butyric acid, it will be possible to prepare the latter free from acetic acid and all impurities except those forming the excretory products of the organism, of which succinic acid appears to be one.

Butyric acid has also been obtained by the fermentation of glycerine in 3 p.c. aqueous solution with a species of schizomyces (Fitz, B. 9, 1348; 10, 276), and has been prepared by various synthetical methods (Frankland and Duppa, A. 138, 218; Geuther and Frélich, A. 202, 306).

*Properties.*—Butyric acid is a colourless, transparent liquid, having an odour resembling that of rancid butter, and a sour burning taste. Cooled to  $-19^{\circ}$  it solidifies, and the crystals melt at about  $-2^{\circ}$ . The acid boils at  $161.5^{\circ}$  at 760 mm. (Kahlbaum, B. 16, 2480); at  $161.5^{\circ}$ – $162.5^{\circ}$  at 753.2 mm. (Brühl, A. 203, 19); at  $162.2^{\circ}$  at 748.7 mm. (Lieben and Rossi, A. 158, 146); at  $162.3^{\circ}$  cor. (Linnemann, A. 160, 228; Zander, A. 224, 64); and has a sp.gr. = 0.9746 at  $0^{\circ}$  (Zander), = 0.9886 at  $0^{\circ}$  and = 0.9580 at  $14^{\circ}$  (Linnemann), and = 0.9587 at  $\frac{20^{\circ}}{4^{\circ}}$  (Brühl).

Butyric acid is inflammable and burns with a blue flame. Alcohol, wood spirit and water dissolve it in all proportions, and from the aqueous solution it can be separated by addition of calcium chloride. Prolonged boiling with nitric acid converts it into succinic acid.

*Salts.*—The metallic salts of normal butyric acid are generally soluble in water, and are crystalline. NaB and KB crystallise in indistinct cauliflower-like groups. AgB crystallises in needles or monoclinic prisms, and dissolves in 200 parts of water at  $14^{\circ}$  (Linnemann and Zolta, A. 161, 177); 100 parts of water dissolve 0.413 part at  $16^{\circ}$  (Grünzweig, A. 162, 203).  $\text{HgB}_2 + 5\text{H}_2\text{O}$  crystallises in very soluble scales (Pelouze and Gélis, A. 47, 249).  $\text{BaB}_2 + 4\text{H}_2\text{O}$  crystallises in nacreous scales and dissolves in 2.48 parts of water at  $14^{\circ}$  (Linnemann and Zolta).  $\text{CaB}_2 + \text{H}_2\text{O}$  crystallises in rhombic forms, and, when anhydrous, dissolves in 100 parts of water to the following amounts: 19.4 parts at  $0^{\circ}$ , 17.56 parts at  $20^{\circ}$ , 15.92 parts at  $40^{\circ}$ , 15.05 parts at  $60^{\circ}$ , 15 parts at  $65^{\circ}$ – $80^{\circ}$ , 15.04 parts at  $85^{\circ}$ , and 15.81 parts at  $100^{\circ}$  (Hecht, A. 213, 72).  $\text{SrB}$  forms monoclinic prisms; 100 parts of water at  $20^{\circ}$  dissolve 39.2 parts of the salt (Grünzweig).  $\text{ZnB}_2 + 2\text{H}_2\text{O}$  forms monoclinic prisms; 100 parts of water at  $16^{\circ}$  dissolve 10.7 parts of the crystallised salt (Grünzweig).  $\text{PbB}_2$  is an oil which slowly solidifies (Markownikow, A. 138, 361).  $\text{CuB}_2 + \text{H}_2\text{O}$  crystallises in triclinic forms (Alth, A. 91, 176), and  $\text{CnB}_2 + 2\text{H}_2\text{O}$  crystallises in monoclinic forms (Pelouze and Gélis).

*Separation from formic, acetic and propionic acids.*—Butyric acid can be separated from its lower homologues by converting the mixed acids into barium salts with baryta, evaporating to dryness, and extracting the residue with absolute alcohol at  $30^{\circ}$ , since at this temperature 100 parts of alcohol dissolve 0.0055 part of barium formate, 0.0284 part of barium acetate, 0.261 part of barium propionate, and 1.1717 part of barium butyrate (Luck, Fr. 10, 185).

Butyryl chloride, obtained by treating 96 grams of butyric acid with 100 grams of phosphorus trichloride (Bueker, A. Ch. [5] 26, 468), boils at  $100^{\circ}$ – $101.5^{\circ}$  (Linnemann), and has a sp.gr. = 1.0277 at  $\frac{20^{\circ}}{4^{\circ}}$  (Brühl).

Butyric anhydride, prepared by the action of butyryl chloride on butyric acid (Linnemann, A. 161, 179), boils at  $191^{\circ}$ – $193^{\circ}$  (L.), and has a sp.gr. = 0.978 at  $12.5^{\circ}$  (Gerhardt, A. 87, 156).

Butyramide, formed by heating dry ammonium butyrate for six hours at  $230^{\circ}$  (Hofmann, B. 15, 982) crystallises in tables, melts at  $115^{\circ}$ , boils at  $216^{\circ}$ , and is readily soluble in water.

Substituted butyric acids have been prepared. Chlorobutyric acids are obtained either by the direct action of chlorine or by oxidation of the corresponding chlorinated aldehydes with nitric acid, and have been described:  $\alpha$ -monochlorobutyric acid, by Markownikow (A. 153, 241);  $\beta$ -monochloro-, by Pinner (B. 12, 2056); dichloro-, by Pelouze and Gélis (A. Ch. [3] 10, 447), and Naumann (A. 119, 120); trichloro-, by Krämer and Pinner (B. 3, 389) and Judson (B. 3, 787); and tetrachloro-, by Natterer (M. 4, 551). Bromobutyric acids can be obtained by the direct action of bromine, and have been described:  $\alpha$ -monobromobutyric acid, by Naumann (L.c.), Wislicenus and Urech (A. 165, 93); dibromo-, by Schneider (J. 1861, 458); and, together with tribromo-, by Michael and Norton (Am. 2, 16).

**Isobutyric acid** ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ ).

**Occurrence.**—Isobutyric acid occurs in the fruit of *Siliquea dulcis* (Grünzweig, A. 162, 190), and in arnica root (*Arnica montana*) (Sigel, A. 170, 348).

**Preparation.**—Isobutyric acid is most readily prepared by the oxidation of isobutyl alcohol with a mixture of sulphuric acid and potassium bichromate. Pierre and Puchot (A. Ch. [4] 28, 366) give the following proportions: isobutyl alcohol (300 parts) is mixed with water (1500 parts) and sulphuric acid (540 parts) and into the well-cooled mixture finely powdered potassium bichromate (400 parts) is gradually introduced. An ethereal layer separates, consisting of isobutylic isobutyrate, which is decomposed by allowing 55 parts to fall slowly on 100 parts of caustic potash to which one-tenth its weight of water has been added; the resulting potassium salt is then distilled with dilute sulphuric acid, and the aqueous acid purified by fractional distillation.

Synthetical methods for preparing this acid have been described by Frankland and Duppa (A. 138, 337), and Markownikow (A. 138, 361).

**Properties.**—Isobutyric acid resembles its isomeride in appearance, but has a less disagreeable odour. It boils at  $152^\circ$  at 760 mm. (Kahlbaum, B. 16, 2480); at  $153.5^\circ$ – $153.8^\circ$  at 750.3 mm. (Brühl, A. 200, 180); at  $154^\circ$ – $154.2^\circ$  (Zander, A. 224, 77); at  $155.5^\circ$  (Pierre and Puchot); and has a sp.gr. = 0.9697 at  $0^\circ$  (P. a. P.); = 0.9651 at  $0^\circ$  (Zander); = 0.9503 at  $20^\circ$  (Linnemann, A. 162, 9). It dissolves in five times its volume of water (L.). The metallic salts of isobutyric acid are more soluble in water than those of the normal acid. The potassium and sodium salts form cauliflower-like masses. AgB crystallises in characteristic tabular forms; 100 parts of water dissolve 0.928 part at  $16^\circ$  (Grünzweig, A. 162, 210).  $\text{MgB}_2$  forms white scales.  $\text{CaB}_2 + 5\text{H}_2\text{O}$  forms four-sided monoclinic crystals; 100 parts of water at  $18^\circ$  dissolve 36 parts of crystallised salt (G.), and the solubility increases as the temperature rises.  $\text{SrB}_2 + 5\text{H}_2\text{O}$ ; 100 parts of water at  $17^\circ$  dissolve 44.1 parts of the crystallised salt (G.).  $\text{BaB}_2 + 4\text{H}_2\text{O}$  forms monoclinic crystals (Fitz, B. 13, 1316).  $\text{ZnB}_2 + \text{H}_2\text{O}$ ; 100 parts of water at  $19.5^\circ$  dissolve 17.3 parts of the crystallised salt (Grünzweig).  $\text{PbB}_2$  crystallises in rhombic tables and dissolves in 11 parts of water at  $16^\circ$ .

**Isobutyryl chloride**, prepared by treating isobutyric acid (12 parts) with phosphorus trichloride (7 parts), and subsequently distilling (Tönnies and Staub, B. 17, 850), boils at  $91.5^\circ$ – $92.5^\circ$  at 748.2 mm., and has a sp.gr. = 1.0174 at  $20^\circ$  (Brühl, A. 203, 20).

**Isobutyryl anhydride**, obtained by boiling isobutyric acid with isobutyryl chloride for twelve hours in a reflux apparatus and fractionating the product (Tönnies and Staub), boils at  $181.5^\circ$  at 734 mm., and has a sp.gr. = 0.9574 at  $16.5^\circ$ .

**Isobutyramide**, formed by heating dry ammonium isobutyrate at  $230^\circ$  for six hours, melts at  $128^\circ$ – $129^\circ$  (Hofmann, B. 15, 982).

Substituted isobutyric acids have been prepared:  $\alpha$ -monochlorisobutyric acid, by Barbiano (B. 11, 1693); trichloro-, by Gottlieb (J. pr. [2] 12, 1); bromisobutyric acids (Markownikow, A. 153, 229; Engelhorn, A. 200, 65, 68; Cahours, A. Suppltd. 2, 349, 352).

**BUTYRIC ETHERS.** These compounds are for the most part prepared by the action of butyric acid on the corresponding alcohols in the presence of some dehydrating agent such as sulphuric acid, the temperature being raised eventually to complete the reaction. Butyric ethers are liquids which dissolve in alcohol and ether in all proportions, but are only very sparingly soluble in water. On saponification with caustic potash they yield the corresponding alcohol and potassium butyrate.

**Methyl butyrate**  $\text{C}_4\text{H}_9\text{O}_2\text{Me}$ , prepared similarly to the ethyl-salt, is a colourless liquid with a pleasant odour resembling that of pine-apples. It boils at  $102.3^\circ$  at 760 mm. (Schumann, P. [2], 12, 41), at  $102$ – $102.5^\circ$  at 761.3 mm. (Schiff, A. 220, 332), and has a sp.gr. = 0.9194 at  $0^\circ$  (Elsässer, A. 218, 314).

**Ethyl butyrate**, *butyric ether*, is prepared by adding 1 part by weight of sulphuric acid to 2 parts each by weight of butyric acid and alcohol. The liquid becomes heated, and the mixture at once separates into two layers of which the upper one consists of ethyl butyrate. To complete the reaction it is necessary to heat the product at about  $80^\circ$  for a short time. The upper layer is separated, washed with water, dried over calcium chloride, and distilled. The presence of considerable quantities of water does not seem to hinder etherification (Pelouze and Gélis, A. 47, 250).

Ethyl butyrate is a colourless liquid having an odour like that of pine-apples. It boils at  $119.9^\circ$  at 760 mm. (Schumann), at  $119.5^\circ$ – $120^\circ$  at 759.4 mm. (Schiff), and has a sp.gr. = 0.8996 at  $0^\circ$  (Elsässer). A solution of ethyl butyrate is very largely used in perfumery and in confectionery under the name of pine-apple oil.

**Propyl butyrate** boils at  $142.7^\circ$  at 760 mm. (Schumann), at  $143$ – $144^\circ$  at 762 mm. (Schiff), and has a sp.gr. = 0.8930 at  $0^\circ$  (Elsässer).

**Isopropyl butyrate** boils at  $129^\circ$  at 755 mm., and has a sp.gr. = 0.8787 at  $0^\circ$  (Silva, B. 2, 283), = 0.9027 at  $0^\circ$  (Fribram and Handl, M., 2, 690).

**Butyl butyrate** boils at  $164.8^\circ$  (cor.), and has a sp.gr. = 0.8760 at  $12^\circ$  (Linnemann, A. 161,

195; compare also Lieben and Rossi, A. 158, 170).

**Isobutyl butyrate** boils at  $156.9^{\circ}$  at 760 mm. (Schumann), at  $157-158^{\circ}$  at 763.2 mm. (Schiff), and has a sp.gr. = 0.8798 at  $0^{\circ}$  = 0.8664 at  $16^{\circ}$  (Grünzweig, A. 162, 207).

**Isoamyl butyrate** boils at  $178.6^{\circ}$  at 760 mm. (Schumann), and has a sp.gr. = 0.8823 at  $\frac{0^{\circ}}{4^{\circ}}$  (Elsässer).

The hexyl- and octyl-butyrate occur in the oils from the fruits of *Heracleum giganteum* (Franchimont and Zincke, B. 4, 824), and *Pastinaca sativa* (Renesse, A. 166, 80), respectively.

Ethereal salts of isobutyric acid have been prepared:

**Methyl isobutyrate** boils at  $92.3^{\circ}$  at 760 mm. (Schumann), at  $92.4^{\circ}$  at 760.7 mm. (Schiff), and has a sp.gr. = 0.9112 (Elsässer).

**Ethyl isobutyrate** boils at  $110.1^{\circ}$  at 760 mm. (Schumann), at  $110.1^{\circ}$  at 757.3 mm. (Schiff). Its sp.gr. = 0.8903 (Elsässer).

**Propyl isobutyrate** boils at  $133.9^{\circ}$  at 760 mm. (Schumann), at  $134.8^{\circ}-135.4^{\circ}$  at 760.3 mm. (Schiff). Its sp.gr. = 0.8843 (Elsässer).

**Isopropyl isobutyrate** boils at  $118^{\circ}-121^{\circ}$  at 727 mm., and has a sp.gr. = 0.8787 at  $0^{\circ}$  (Pflibram and Handl).

**Isobutyl isobutyrate** boils at  $146.6^{\circ}$  at 760 mm. (Schumann), at  $147.5^{\circ}$  at 760 mm. (Kahlbaum), at  $148.5^{\circ}-149.5^{\circ}$  at 759.2 mm. (Schiff). Its sp.gr. = 0.8752 (Grünzweig).

**Isoamyl isobutyrate** boils at  $168.8^{\circ}$  at 760 mm. (Schumann), and has a sp.gr. = 0.8759 at  $\frac{0^{\circ}}{3^{\circ}}$  (Elsässer).

**BUTYRALDEHYDE** *Butyric aldehyde*  $C_4H_8O$ . This compound exists in two isomeric forms, termed normal and isobutyric aldehyde respectively.

**Normal butyraldehyde**  $CH_3(CH_2)_3CHO$  is formed together with acetaldehyde and propaldehyde by the action of chromic acid upon fibrin, casein and albumen (Guckelberger, A. 64, 39). It is readily prepared by distilling a mixture of calcium formate (2 mol.) and calcium butyrate (1 mol.) in quantities of 50 grams at a time with twice the weight of iron filings. The distillate is fractionated, the fraction  $70^{\circ}-110^{\circ}$  treated with sodium hydrogen sulphite (bisulphite), then shaken with ether to extract impurities, and finally distilled with excess of soda (Lipp, A. 211, 355; Linnemann, A. 161, 186; Kahn, B. 18, 3364).

**Properties.**—Normal butyraldehyde is a liquid which boils at  $73^{\circ}-74^{\circ}$  (Lipp), at  $73^{\circ}-77^{\circ}$  and has a sp.gr. = 0.8170 at  $\frac{20^{\circ}}{4^{\circ}}$  (Brühl, A. 203, 18). It is soluble in 27 parts of water. With sodium hydrogen sulphite (bisulphite) it unites, yielding a crystalline compound (Justin, B. 17,

2505; Kahn). When treated with aqueous ammonia at  $0^{\circ}$  it yields butyraldehyde-ammonia  $C_4H_7NO + 3\frac{1}{2}H_2O$ , which crystallises in acute rhombic tetrahedra and melts at  $30^{\circ}-31^{\circ}$  (Guckelberger). If, however, alcoholic ammonia and the aldehyde are allowed to stand for a month, and then heated for a day at  $100^{\circ}$ , condensation occurs, and, after removal of ammonia, alcohol and unattacked butyraldehyde by distillation, two bases, tetrabutryaldine and dibutryaldine  $C_8H_{15}NO$  can be separated by fractional precipitation with platinic chloride. The latter only can be crystallised, and when heated is converted into paraconine  $C_8H_{15}N$  and water (Schiff, A. 157, 352). The trichlorobutyraldehyde (butylehloral) and its hydrate have been prepared by Pinner (A. 179, 26).

**Isobutyraldehyde**  $(CH_3)_2CH.CHO$  can be prepared by the oxidation of isobutyl alcohol with potassium bichromate and sulphuric acid (Lipp, A. 205, 2; Pinner, B. 5, 699; Fossek, M. 2, 614; 4, 661), or by distilling calcium formate with calcium isobutyrate (Linnemann and Zotta, A. 162, 7). It dissolves in 9 parts of water at  $20^{\circ}$ , and is soluble in alcohol and ether. The boiling-point is  $61^{\circ}$  (Pierre and Puchot, A. 163, 286),  $63^{\circ}-64^{\circ}$  at 757 mm. (Brühl, A. 203, 18),  $63^{\circ}$  at 741 mm. (Fossek), and the sp.gr. = 0.7911 at  $27.8^{\circ}$  (Pierre and Puchot), = 0.7938

at  $\frac{20^{\circ}}{4^{\circ}}$  (Brühl), = 0.8057 at  $0^{\circ}$ , and = 0.7898 at  $20^{\circ}$  (Fossek), = 0.79722 at  $15^{\circ}$  (Perkin, C. J. 45, 476). Condensation compounds have been obtained by Perkin (C. J. 43, 91), Barbaglia (B. 5, 1052), Fossek (*l.c.*), and Urech (B. 12, 1745).

**BUTYRONE** *Dipropyl ketone*  $C_7H_{14}O$ .

Butyrene is obtained by distilling calcium butyrate, or preferably a mixture of calcium butyrate and calcium carbonate (Schmidt, B. 5, 597); the crude product is dehydrated by treatment with calcium chloride, and purified by fractional distillation. Butyrene boils at  $144^{\circ}$ , and has a sp.gr. = 0.8195 at  $20^{\circ}$ , does not combine with ammonia and sodium hydrogen sulphite (bisulphite), yields a mixture of propionic and butyric acids on oxidation with chromic acid, and is converted into a secondary alcohol  $C_7H_{14}O$  and butyrene-pinacone  $C_{11}H_{20}O_2$  on treatment with sodium amalgam and water (Kurtz, A. 161, 205).

An isomeride *di-isopropylketone* can be prepared by distilling calcium isobutyrate (Münch, A. 180, 327); it boils at  $124-126^{\circ}$ , has a sp.gr. = 0.8254 at  $17^{\circ}$ , and does not combine with sodium hydrogen sulphite.

**BUXIN.** An alkaloid obtained from the box-tree (*Buxus sempervirens*). Hager (C. C. 1877, 119) found it in beer as an adulterant. It is said by Walz (N. J. P. 14, 15) to be identical with bebecrine *v.* VEGETO-ALKALOIDS.



## C

CADAVERINE *v.* PTOMAINES.CADIE GUM *v.* GUMS.CADMIUM. (*Kadmium*, Ger.) Symbol Cd.  
At. wt. 111.7 (Hauer, Dumas).

Cadmium occurs in small quantities as sulphide in *Greenockite* at Bischopton, Renfrewshire, and in Pennsylvania and Bohemia. This is the only ore containing cadmium as the principal element. Cadmium occurs in small quantities in nearly all zinc ores, those of Silesia containing as much as 5 p.e. The radiated zinc blende of Przibram, Hungary, contains from 2 to 3 p.e. Calamine occurs at Eaton, N. America, containing 3 p.e. of cadmium. It occurs also in the silicate and carbonate of zinc at Freiberg, Derbyshire, and Cumberland, and in most commercial zinc.

*Preparation.*—In the reduction of zinc ores the more volatile cadmium passes over in the first portions of the distillate. This, when containing sufficient cadmium, is collected for the extraction of that metal. At Silesia, the first portion of the distillate, which contains from 2 to 11 p.e. of cadmium, is mixed with about one-fourth of its weight of coal, and distilled at a dull red heat; the cadmium then distils with a little zinc, but the greater part of the latter metal remains behind. After being again distilled, the metal, thus nearly freed from zinc, is cast into small cylinders about  $\frac{1}{2}$  inch thick.

In some cases the metal obtained by the redistillation of the first crude product with coal is dissolved in hydrochloric acid, and the cadmium precipitated from the diluted solution by the addition of metallic zinc. The spongy metal so produced is fused and cast into ingots. For the preparation of cadmium free from zinc the metal is dissolved in hydrochloric acid, diluted, and precipitated as sulphide by a current of sulphuretted hydrogen. The sulphide is filtered off, dissolved in strong hydrochloric acid, and the cadmium precipitated as carbonate by the addition of sodium carbonate, which on ignition yields the oxide; from this the metal is produced by distillation with charcoal as before.

*Properties.*—Cadmium is a white metal with a tinge of blue, of strong lustre, and capable of taking a high polish. It produces a metallic streak on paper like lead, but less readily. Cadmium is compact in texture and of fibrous fracture, harder and more tenacious than tin, it may be drawn into thin wire or hammered into leaves, but when heated to 80°C. it becomes brittle, and may be powdered in a mortar. On account of its crystalline structure it crackles, like tin, when bent.

By distillation in a current of hydrogen, cadmium may be produced in regular octahedra and other figures of the cubic system.

Cadmium melts at 320°C. (Van Riemsdijk), and boils at 763–772°C. (Carnelley and Carlton Williams). Its vapour density at 1,010°C. is 3.94 referred to air, or 56.3 referred to hydrogen. Hence it appears that the molecule of cadmium contains but one atom at that temperature.

According to Demarcay, it emits vapours when heated below the melting-point (C. R. 95, 183). When heated in air it burns readily, evolving brown fumes of the oxide. Cadmium dissolves in hydrochloric and sulphuric acids with evolution of hydrogen. It is readily attacked by nitric acid. It combines directly with chlorine, bromine, and iodine when placed in solutions of those elements. According to Alberta (J. 1865, 242) the presence of platinum increases its solubility in such solutions and in acids.

*Detection.*—All compounds of cadmium, when heated on charcoal in the reducing flame, give a brown incrustation. Sulphuretted hydrogen produces a yellow precipitate in acid solutions, soluble in strong hydrochloric acid, insoluble in alkaline sulphides; it is thus distinguished from antimony and arsenic.

*Estimation.*—Cadmium is best precipitated as carbonate by the addition of sodium carbonate. The well washed and dried precipitate is then detached as far as possible from the filter paper and converted into oxide in a porcelain crucible; the filter paper is saturated with nitric acid or solution of ammonium nitrate, dried and ignited on the lid of the crucible; in this way the loss from reduction of the oxide to the volatile metal is minimised. The crucible and contents with the lid are then weighed, and the percentage of cadmium calculated from the weight of oxide produced.

For the separation from other metals not precipitable by sulphuretted hydrogen in acid solution, it is precipitated as sulphide by that gas, washed, dissolved in nitric acid, and precipitated as above with sodium carbonate.

*Alloys of cadmium.* The addition of cadmium to metals usually increases their fusibility without destroying their malleability.

An alloy of 100 copper and 82 cadmium is yellowish-white and of fine-grained scaly structure. One part of cadmium with 2 of silver produces a strong malleable alloy; 100 parts of platinum with 117 of cadmium form a very brittle, silvery white, fine-grained alloy, refractory in the fire (Stromeyer). With mercury it forms hard, silver-white amalgams; the alloy containing 21.7 p.e. of cadmium crystallises in octahedra. An amalgam of cadmium and mercury frequently containing tin is used in dentistry. For fusible and other alloys containing bismuth and cadmium *v.* *Alloys of bismuth*, art. BISMUTH.

Cadmium oxide CdO is prepared by heating the carbonate, in which case it is of a pale brown colour; or by igniting the nitrate, when it is much darker and forms minute crystals. By heating cadmium in a current of oxygen the oxide may be condensed in octahedral crystals. Cadmium oxide is infusible, insoluble in water, soluble in acids. It constitutes the brown deposit found in the condensers in the distillation of zinc.

Cadmium chloride CdCl<sub>2</sub> is prepared by dissolving the metal or oxide in hydrochloric acid, and evaporation. It melts below a red heat and

sublimes at a higher temperature, condensing in micaceous plates.

**Cadmium iodide**  $\text{CdI}_2$  is obtained by digesting 1 part of the metal with 2 parts of iodine in water and evaporating the solution. It crystallises in large transparent tablets, soluble in water and alcohol. It is used in medicine and, on account of its stability and solubility in alcohol, for iodising collodion plates in photography.

**Cadmium sulphide.** *Cadmium yellow.* *Jaune brillant.* This pigment may be produced by the addition of sulphuretted hydrogen or an alkaline sulphide to a solution of a cadmium salt. It may also be prepared by heating a mixture of cadmium oxide and excess of sulphur, but that produced by the former method is of a finer colour and has greater covering power.

It is an orange or lemon-yellow powder, but may be obtained in prismatic crystals. When heated to redness it becomes first brown, then earmine; it melts at a bright-red heat, and solidifies on cooling in laminae of the original colour.

It is a very brilliant permanent colour. According to Jacquet it is acted upon by light and by chlorine. It is much used as an oil and water colour, for colouring certain toilet soaps, for the production of a blue flame in pyrotechny, and in calico-printing. The chief adulterants are compounds of zinc. According to Buchner (C. Z. 11, 1,087 and 1,107) two modifications of cadmium sulphide exist; the lemon-yellow ordinary sulphide, and a polymericide of a vermilion colour, which becomes permanently yellow if heated. The various shades of the pigment are produced by the combination of these two colours.

The red variety is produced when the solution precipitated by sulphuretted hydrogen is acid. From a dilute solution of a cadmium salt sodium sulphide precipitates the yellow modification; from a strong solution a reddish mixture of the two modifications; and from a strong boiling solution, a brick red precipitate.

Schmid (D. P. J. 241, 149) prepares a steam yellow for calico-printing as follows: 16 parts wheaten starch and 40 parts burnt starch are boiled in 1,000 parts of water and mixed while hot with 350 parts of sodium thiosulphate. To the cooled solution 350 parts of finely powdered cadmium nitrate are added with constant stirring until dissolved. This solution does not react in the cold, and may be applied to the fabric and steamed, the yellow sulphide being then precipitated.

**Cadmium sulphate**  $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$  is a very soluble salt prepared by dissolving the oxide or carbonate in sulphuric acid. It is used to some extent in medicine, especially on the Continent.

**Cadmium nitrate**  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  is prepared by dissolving the oxide or carbonate in nitric acid. It crystallises in deliquescent fibrous needles, soluble in alcohol.

**CÆSIUM.** Symbol Cs. At. wt. 132.7 (Bunsen; Johnson and Allen). Cesium was discovered in 1860 by Bunsen and Kirchhoff, in the Dürkheim water, being the first metal discovered by means of the spectroscope.

It is widely but sparsely distributed, usually in association with rubidium, as in the *lepidolite*

from Hebron, in Maine, U.S.A., which contains 0.4 p.e. cesium oxide and 0.2 p.e. rubidium oxide; in *petalite*; in the mother liquors of the Nauheim salt spring, and in the ash of sea-weed, tobacco, tea, and other plants. Setterberg (A. 210, 100) describes a method for the separation of cesium and rubidium from the alums obtained as a by-product in the manufacture of lithia from lepidolite.

Cesium occurs free from rubidium in the rare mineral *pollux*, from Elba, to the extent of 34 p.e. of cesium oxide; to the extent of 1.71 parts of cesium chloride per million in the water of the Wheal Clifford Mine (Yorke) and in the mineral waters of Frankhausen.

Cesium may be prepared by electrolysis of a fused mixture of cesium cyanide 4 parts and barium cyanide 1 part, using electrodes of aluminium (Setterberg). It resembles rubidium and potassium in appearance, being silvery white, and soft at ordinary temperatures. It quickly oxidises in air, and rapidly decomposes water with ignition of the liberated hydrogen. Its sp.gr. at 15° is 1.88, its melting-point is 26–27°C. (Setterberg).

Cesium is the most electro-positive of all the elements. Its salts are stable, and have a strong tendency to form double salts. The salts are isomorphous with those of potassium and rubidium, and impart a more reddish tinge to the Bunsen flame than salts of those metals. The hydroxide  $\text{CsHO}$  is a greyish-white highly deliquescent solid, melting below a red heat. The anhydrous oxide has not been prepared.

**CAFFEINE** v. **VEGETO-ALKALOIDS.**

**CAFFEONE.** A brown oil, heavier than water, and slightly soluble in boiling water. Constitutes the aromatic principle of coffee. May be obtained by distilling freshly roasted coffee with water, and agitating the distillate with ether which attracts the oil.

**CAIL-CEDRA.** *Kaya senegalensis* or *Swietenia senegalensis*. A tree of the cedrelaceous order, growing on the banks of the Gambia and on the lowlands of the peninsula of Cape de Verde. Its bark is very bitter, and is much prized by the natives as a febrifuge, on which account it has been called the *cinchona* of Senegal. Its wood resembles mahogany (*Swietenia mahoganii*), and is used in making the finer kinds of furniture. The bark contains, amongst other substances, an extremely bitter, neutral resinous substance called cail-cedrin, to which its active properties appear to be due.

Cail-cedrin is very sparingly soluble in water, but readily soluble in alcohol, ether, and chloroform. It is obtained by repeatedly exhausting the coarsely pulverised bark with boiling water; evaporating the filtered liquids over the water-bath to the consistence of a syrup; exhausting this extract with alcohol of 90 p.e.; precipitating the alcohol filtrate with basic lead acetate; filtering, distilling off the alcohol, and agitating the residue with chloroform, which dissolves nothing but the bitter principle. 1 kilogram of the bark yields about 8 milligrams of cail-cedrin (Caventon, J. Ph. [3] 16, 353; 33, 123).

**CAINCETIN** v. **GLUCOSIDES.**

**CAINCIN** v. **GLUCOSIDES.**

**CAIRNGORM.** A yellow or pale brown transparent variety of quartz, largely used as an

ornamental stone. A rich yellow tint is often produced artificially by the action of heat upon dull, smoky quartz. The mineral derives its name from Cairngorm (the Blue Mountain), one of the highest peaks of the Central Grampians. Most of the cairngorm of commerce is now obtained from Spain or from Brazil. Certain cairngorms bear a strong resemblance to yellow topaz, and are hence known to jewellers as 'Scotch topaz' or 'Spanish topaz.' The simplest way of distinguishing such false topaz from the true stone is to take its specific gravity (cairngorm 2.6, topaz 3.5). When determinations have to be made frequently, it is convenient to have Sonstadt's solution made up to a density of nearly 3. On dropping the stones into such a solution, the true topaz sinks while the cairngorm floats.

F. W. R.

**CAJEPUT OIL** *v.* OILS, ESSENTIAL.

**CAJEPUTOL** *v.* CAMPHORS.

**'CAL'** *v.* TUNGSTEN.

**CALABARINE** *v.* VEGETO-ALKALOIDS.

**CALAMINE.** A term applied indifferently to both silicate and carbonate of zinc. In this country the term is usually restricted to the carbonate, whilst the silicate is called *Smithsonite* or electric calamine (*v.* ZINC).

**CALAMUS.** The Indian variety of *Acorus calamus*; is used as a medicine in the Levant; the Turks candy it and employ it as a remedy against contagion. The volatile oil occasionally enters into the composition of aromatic vinegar. According to Thoms cleorin  $C_{36}H_{60}O_6$  in contact with ferments splits up into sugar and oil of calamus  $C_{36}H_{60}O_6 = C_6H_{12}O_6 + 3C_{10}H_{16}$  (*v.* ACORUS CALAMUS).

**CALCIUM.** Symbol Ca. At. wt. 39.9. Lime, the oxide of calcium, has been employed in the preparation of mortar from very early times. Interesting accounts of the process of lime-burning are given by Dioscorides and Pliny. It was not, however, until 1756 that the difference between burnt and unburnt lime was pointed out by Black. In 1808 the metal itself was first isolated by Davy, and has since been obtained in the pure state by Matthiessen.

Calcium is universally found as carbonate  $CaCO_3$  in the forms of *calespar*, *marble*, and *limestone*, often in whole mountain ranges or immense coral reefs. *Dolomite* or *bitter spar*, the double carbonate of calcium and magnesium, constitutes the geological formation termed magnesium limestone. Calcium sulphate as *anhydride*  $CaSO_4$  or *selenite* (*gypsum*)  $CaSO_4 \cdot 2H_2O$ , is also very plentiful. The phosphate united with the chloride or fluoride also occurs widely distributed, often as minute inclosures in crystals of the primary rocks, as the mineral *apatite*, while calcium is an important base in the greater number of natural silicates. The solid matter carried away by rivers largely consists of the carbonate and sulphate of calcium, while sea-water contains, in addition to these, both phosphate and fluoride of calcium. The bones of animals consist largely of calcium phosphate, and the shells of molluscs of the carbonate. Calcium salts are never absent from plant tissues, concentrating mainly in the leaves.

Calcium also occurs in extra-terrestrial bodies, in the sun, meteorites, and many fixed stars.

*Preparation of the metal.*—Calcium was obtained as an impure metallic powder by Davy in 1808 by the electrolysis of the chloride, using mercury as negative electrode, and afterwards heating the amalgam thus formed until the mercury was volatilised. It was obtained as a metallic solid by Matthiessen in 1856 (C. J. 8, 28) in the following manner:—A mixture of calcium and strontium chlorides in the proportion of two molecules to one, together with a little ammonium chloride, the whole being more readily fusible than pure calcium chloride, was melted in a porcelain crucible in which was inserted a carbon positive pole. A thin pianoforte wire wound round a thicker one, and dipping just below the surface of the fused mass, constituted the negative pole. On passing the electric current, beads of metallic calcium attached themselves to the fine wire, and were separated by withdrawing the negative pole every few minutes. The surest way of obtaining the metal by this process is to only permit the negative pole, which should, under these circumstances, be pointed, to graze the surface of the fused mixture; the heat occasioned by the resistance effects the fusion of the metal, which drops off the point of the wire in beads which may be ladled out with an iron spatula.

Liës-Bodart and Gobin (C. R. 47, 23) obtained calcium by heating the iodide with an equivalent of sodium in an iron crucible, the lid of which was screwed down. Dumas (C. R. 47, 175) states that a closed vessel is necessary in this process.

Frei obtained calcium in globules weighing 2.4 to 4 grams by the electrolysis of the chloride.

Another process consists in fusing 3 parts of calcium chloride with 4 parts of zinc and 1 part of sodium, thus forming an alloy of zinc and calcium, which, when heated in a gas-carbon crucible, decomposes, the zinc volatilising and a button of fused calcium remaining (Caron A. 115, 355).

Calcium is a light yellow metal resembling an alloy of gold and silver, lustrous when freshly cut, and giving a yellow streak. It has a hardness about the same as that of gold, and, like that metal, is very ductile and malleable, being readily hammered out into very thin sheets. Its specific gravity is 1.5778. Perfectly dry air is without sensible action upon it, but in moist air it rapidly becomes converted into hydrate. Heated on platinum foil in the air it burns with a bright yellow flash, and if thrown into water produces a violent evolution of hydrogen. Heated in chlorine it burns brilliantly, forming the chloride; bromine and iodine, oxygen and sulphur, also combine with it at moderately high temperatures with evolution of light. Strong nitric acid is without action below its boiling-point, but dilute nitric acid acts so violently that ignition frequently occurs. Dilute hydrochloric and sulphuric acids also rapidly dissolve the metal. According to Mallet, lime heated with aluminium in a wind-furnace forms calcium which volatilises.

Calcium unites with all the non-metallic elements forming compounds, into which it enters as a divalent radicle; the compounds are generally colourless, of acid taste, and



lower specific gravity than those of the other alkaline-earth metals.

Fused with a large excess of zinc, calcium forms an alloy of the composition  $\text{CaZn}_{12}$ , which crystallises in quadratic octahedrons of sp.gr. 6.37; it is decomposed by water (G. vom Rath, Z. [2] 5, 665).

**Calcium oxide**, lime,  $\text{CaO}$ . Anhydrous calcium oxide is obtained by heating to redness any salt of calcium containing a volatile acid, as the carbonate and nitrate. Calcium carbonate, when heated in a closed vessel, may be fused without decomposition, but when raised to a red heat under ordinary pressure, it gives off its carbon dioxide, and becomes converted into lime:  $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ .

To obtain pure lime, Iceland spar or other forms of calcite, or the finest marble, may be employed, the ignition being performed in a crucible with perforated base so as to permit of the entrance of furnace gases, which carry away the carbon dioxide as fast as it is formed; otherwise the decomposition is incomplete, the carbonate undergoing no change in an atmosphere of  $\text{CO}_2$ .

Lime is prepared on the large scale by burning chalk or limestone (impure carbonate) in egg-shaped kilns. The limestone is brought to the mouths of the kilns in waggons, generally in lumps a little larger than paving sets. In the older kilns an arch is first formed over the firegrate at the bottom with a number of the larger lumps, the rest of the kiln being filled up with smaller pieces well mixed with coal or other combustible material; the fire is then kindled and kept up for about two days and nights, after which the kiln is allowed to cool and the lime subsequently removed. In the more modern continuous process, the limestone is from time to time renewed at the top and the burnt lime removed at the base; a waggon load of limestone, then a charge of coal, being supplied one after the other as fast as the burnt lime is extracted by the furnace men below. The kilns are generally arranged in rows, so that a train of waggons may be employed in continuously removing the lime. By this method of working a great saving of fuel is effected, and the smoke, so offensive in the older forms of kilns, is greatly reduced, being drawn into a central chimney and for the most part consumed. About one bushel of coal is required to make five or six bushels of lime, but dolomitic (magnesian) limestones require less. If much argillaceous matter is present, the limestone more readily fuses, and in such cases great care requires to be exercised in order to keep the temperature below the melting-point, otherwise the mass vitrifies, and the lime resulting is said to be 'dead burnt.' The kilns in which such limestones are burnt are usually provided with dampers. Such lime, if not heated too much, slakes slowly, and is termed 'poor lime,' while pure limes, which slake readily, are called 'fat' or 'rich' limes.

Pure calcium oxide forms white porous amorphous masses of sp.gr. 2.3 to 3.08, highly infusible, melting only in the highest temperature of the oxyhydrogen blowpipe flame or in the electric arc. In the ordinary oxyhydrogen flame it emits an intense light, which is much used for lantern projection.

Calcium oxide has been obtained by Brühlmann in minute cubic crystals of sp.gr. 3.251 by heating the nitrate in a porcelain flask (P. [2] 2, 466; and [2] 4, 277).

A crystalline mass found upon the lining of a continuous limekiln at Champigny after twenty-eight months' continuous work was also shown to consist of small cubical crystals of pure lime, of sp.gr. 3.32 (Levallois and Meunier, C. R. 90, 1,566).

Amorphous lime takes up water with remarkable avidity, forming calcium hydroxide  $\text{Ca(OH)}_2$ , the combination being accompanied by a contraction in volume. When a small quantity of water is added to a mass of burnt lime it speedily becomes sufficiently hot to drive off considerable volumes of steam, the mass crumbling at the same time to powder, and becoming what is known as 'slaked lime.' On exposure to air, the amorphous variety of lime rapidly absorbs water and carbon dioxide; the crystalline variety, however, absorbs these constituents of the atmosphere much more slowly. Dilute cold acids are almost without action upon the crystals, but on warming they are readily converted, like amorphous lime, into the several salts with evolution of heat.

**Calcium hydroxide**, hydrate of lime,  $\text{Ca(OH)}_2$ , is obtained by slaking fresh well-burnt quicklime with about a third of its weight of water. It forms a white amorphous powder of sp.gr. 2.078, sparingly soluble in water, and less so in hot than in cold water, as seen from the following table:—

Temperature	Parts of water required to dissolve one part $\text{CaO}$	Temperature	Parts of water required to dissolve one part $\text{CaO}$
0°	759	55°	1,104
5°	764	60°	1,136
10°	770	65°	1,208
15°	779	70°	1,235
20°	791	75°	1,313
25°	831	80°	1,362
30°	862	85°	1,388
35°	909	90°	1,579
40°	932	95°	1,650
45°	985	99°	1,650
50°	1,019		

(Maben, Ph. [3] 14, 505).

The solution known as lime-water has an alkaline reaction, and absorbs the carbon dioxide of the atmosphere, forming a pellicle of carbonate of lime. As the presence of calcium carbonate interferes with the solubility, in order to prepare lime-water of definite strength for pharmaceutical purposes, the lime used must be fresh, and should have been kept out of contact with air as much as possible, and the lime-water, when prepared, ought to be stored in well-stoppered bottles. In preparing lime-water from ordinary lime, the first solutions should invariably be rejected, as they will contain nearly all the soluble salts of the alkalis and the baryta and strontia present in the lime as impurities. Milk of lime is an emulsion of calcium hydrate suspended in less water than is required for its complete solution.

Calcium hydroxide is also precipitated by caustic potash or soda from strong solutions of the chloride; if a saturated solution of calcium chloride be employed the whole becomes solid.

A solution evaporated over sulphuric acid in a vacuum deposits hexagonal prisms, according to Gay-Lussac. Crystals, however, which had separated on the surface of samples of hydraulic cement were found by Glinka (*J. R.* 1885, 451) to belong to the rhombic system in spite of their hexagonal appearance. A deposit of grey lamellæ, consisting of calcium hydroxide, was found by Lucdecke (*Z. K.* 11, 255) in a Carré ice machine.

At a red heat calcium hydroxide is decomposed, water being driven off and oxide remaining.

Slaked lime is greatly used in the preparation of mortars and cements (*v.* CEMENTS), and the oxide is of frequent use in the laboratory as a drying-agent.

Peroxide of calcium  $\text{CaO}_2$  was first prepared by Thenard by the action of excess of hydrogen peroxide upon lime-water, when microscopic quadrate plates of the composition  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ , sparingly soluble in water and insoluble in alcohol, were precipitated. According to Conroy (*C. J.* 1873, 810) the peroxide is most conveniently prepared by adding lime-water in considerable excess to an aqueous solution of sodium peroxide acidulated with nitric acid. It is also obtained as a finely divided white precipitate on adding a neutral or alkaline solution of sodium peroxide to a solution of a calcium salt. The crystals are isomorphous with those of hydrated barium peroxide. On exposure to air they effloresce, and when heated to  $130^\circ$  are converted into the anhydrous peroxide. On increasing the heat half the oxygen is driven off, leaving a residue of pure lime.

Calcium chloride  $\text{CaCl}_2$  is found in the water of nearly all springs and rivers, and is consequently a constituent of the saline matter dissolved in sea-water. This salt also forms the chief saline constituent of an exudation occurring on the face of the old red sandstone rocks at Guy's Cliff, in Warwickshire, occurring to the extent of 27.15 p.c. (Spiller, *C. J.* 1876, 1, 151). Calcium chloride likewise occurs, together with magnesium chloride and alkaline chlorides in the *tachydrite* and *carnallite* of the Stassfurt deposits, *tachydrite* containing 21 p.c.  $\text{CaCl}_2$  and 36 p.c.  $\text{MgCl}_2$ , while *carnallite* contains 3 p.c.  $\text{CaCl}_2$ , and 31 p.c.  $\text{MgCl}_2$ .

Calcium chloride is obtained by passing chlorine over the red-hot oxide, or by dissolving lime, chalk, or marble in hydrochloric acid and evaporating. If it is necessary to obtain the salt pure, chlorine water may be added to the solution in hydrochloric acid in order to oxidise any iron present, which may then be precipitated by the addition of milk of lime, and filtered off. The slightly alkaline filtrate is then acidified with hydrochloric acid and evaporated to the crystallising point.

Calcium chloride is obtained in large quantities as a by-product in many manufacturing processes, notably in the preparation of potassium chlorate and in the manufacture of

sodium carbonate by the ammonia-soda process; it may be obtained in the pure state from these crude products by the method just indicated. Many attempts have been made to utilise this waste calcium chloride. Richardson (*Pat.* 10,418) treats the purified crude solution with ammonium sulphate in the proportion required to convert all the chloride into sulphate; the calcium sulphate could then be filtered off, and ammonium chloride recovered by crystallisation. Webster (*Pat.* 12,344) runs the calcium chloride liquor into a vat, and adds as much slaked lime or powdered chalk or marble as will absorb the liquor so as to form on stirring a paste of the consistency of mortar. This is then dried in a furnace at temperatures gradually approaching  $250^\circ\text{F.}$ , and the dried mass again immersed in the liquor, dried again and immersed a third time. In three operations the mass absorbs the greatest possible amount of calcium chloride; the resulting substance is next melted and cast into blocks for use as a flux in metallurgical operations. If it is to be used for refining iron or in a puddling furnace, 20 p.c. peroxide of manganese is added.

Saturated solutions of calcium chloride deposit the hydrated salt in large hexagonal prisms with pyramidal summits of the composition  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . The crystals melt at  $29^\circ\text{C.}$  in their water of crystallisation and deliquesce rapidly in the air, forming a viscous fluid formerly termed *oleum calcis*. Heated below  $200^\circ\text{C.}$ , or in a vacuum over sulphuric acid, the crystals lose 4 molecules of water. The remaining 2 molecules can only be expelled above  $200^\circ$ . According to Weber (*B.* 15, 2,316), the salt dried at  $180$ – $200^\circ$  is practically anhydrous, containing only 0.2 p.c. of water. Besides the two hydrates above described, Lescœur (*C. R.* 92, 1,158), from determinations of maximum tensions of solutions, shows the probable existence of two others  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 11\text{H}_2\text{O}$ . The tetrahydrate, however, can only exist below  $129^\circ$ .

Anhydrous calcium chloride is a white porous mass, which fuses at a red heat or according to Le Chatelier (*Bl.* 47, 300)  $755^\circ$ . On cooling the salt solidifies to a translucent mass of crystals of sp.gr. 2.205. A slight decomposition into oxide and carbonate occurs when the fusion is performed in air. On this account the porous chloride obtained by drying the crystals at  $200^\circ$  is better adapted for desiccating purposes, especially for the absorption of water in organic analysis. If the fused mass is exposed to the sun's rays it becomes phosphorescent in the dark, and was formerly called *Homborg's phosphorus*, after the discoverer of the fact in 1693.

Anhydrous calcium chloride is highly deliquescent. 100 parts of the powder exposed to an atmosphere saturated with aqueous vapor absorb 124 parts of water in ninety-six days. According to Kromers (*P.* 103, 57; 104, 133; *J.* 1858, 40), the following quantities of water are required to dissolve one part by weight of the anhydrous salt:

$\Delta$ 10-2°	20°	40°	60°
1.58	1.35	0.83	0.72.

In the following table, drawn up by the same author, are shown the specific gravities of solutions of varying strengths:—

Quantities in 100 parts water	Specr. of solutions at 19.5° (water at 19.5°=1)
6.97	1.0545
12.58	1.0954
23.33	1.1681
36.33	1.2469
50.67	1.3234
62.90	1.3806

According to Engel (Bl. 47, 318), 100 parts of water at 0° dissolve 60.3 parts  $\text{CaCl}_2$ , forming a solution of sp.gr. 1.367.

A solution of 50 parts anhydrous  $\text{CaCl}_2$  in 100 parts water boils at 112°, one containing 200 p.c. boils at 158°, and a 325 p.c. solution boils at 180°.

According to Lefebvre (C. R. 70, 684) a supersaturated solution of calcium chloride is formed by dissolving 350–400 grams of the crystallised salt in 50 c.c. warm water or 200 grams of the anhydrous salt in 250 c.c. water; it may be shaken after cooling without crystallisation, but solidifies on contact with a crystal of the salt. If cooled to 5.8° this solution begins to crystallise, the temperature rising to 28–29°. A solution containing 55 p.c.  $\text{CaCl}_2$  deposits at about 15° large plates of the tetrahydrate  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ , which do not induce the crystallisation of the supernatant liquor. This solution, in passing from liquid to solid state, undergoes at 70° a contraction 0.6832 of its volume.

The crystallised chloride  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  also deliquesces rapidly, and dissolves in half its weight of water at 0°, in one-fourth its weight at 16°, and in all proportions of hot water. In dissolving it absorbs heat, while the anhydrous chloride dissolves with evolution of heat. A mixture of 1.44 parts crystallised chloride with 1 part of snow produces a cold of  $-54.9^\circ$ , more than sufficient to freeze mercury.

Both the anhydrous and hydrated chloride dissolve readily in alcohol, 10 parts at 80°C. dissolving 6 parts anhydrous  $\text{CaCl}_2$ ; on evaporation in a vacuum at winter temperature rectangular plates of  $2\text{CaCl}_2 \cdot 7\text{C}_2\text{H}_5\text{O}$  are deposited.

Anhydrous calcium chloride absorbs ammonia gas, forming the compound  $\text{CaCl}_2 \cdot 8\text{NH}_3$  as a white powder, which, on exposure to air, solution in water, or on heating, is decomposed. Thrown into chlorine gas the compound takes fire.

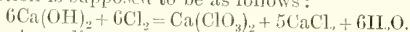
**Calcium oxychloride.** When calcium chloride solution is boiled with slaked lime, and the liquid filtered, white needle-shaped crystals of calcium oxychloride separate out on cooling of the composition  $\text{ClCaO} \cdot \text{Ca}(\text{OH}) \cdot 7\text{H}_2\text{O}$  or  $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$  (Grimshaw, C. N. 30, 280). The salt is stable out of contact with air, loses part of its water of crystallisation over sulphuric acid or caustic lime, and absorbs carbon dioxide from the atmosphere. It is decomposed by water or alcohol.

According to André (C. R. 92, 1,452) the composition of the salt is  $\text{CaCl}_2 \cdot 3\text{CaO} \cdot 16\text{H}_2\text{O}$ , and, on drying in a vacuum it becomes converted into  $\text{CaCl}_2 \cdot 3\text{CaO} \cdot 3\text{H}_2\text{O}$ .

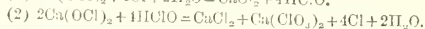
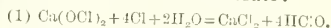
When calcium chloride is fused at a bright-red heat in a current of moist air, it is gradually converted to an oxychloride of the composition  $\text{CaCl}_2 \cdot \text{CaO}$ , and eventually to oxide (Gorgeu, C. R. 99, 256).

**Calcium hypochlorite v. BLEACHING POWDER.**

**Calcium chlorate**  $\text{Ca}(\text{ClO}_3)_2$  is produced when chlorine is passed into hot milk of lime, but is difficult to separate from the chloride simultaneously formed. This is the first step in the manufacture of potassium chlorate, and the reaction is supposed to be as follows:



According to Lunge (S. C. I. 1885, 722) the reaction really takes place in several stages, calcium hypochlorite and hypochlorous acid being first formed and mutually reacting with production of calcium chlorate:



The free chlorine serves only as carrier of the oxygen of two molecules calcium hypochlorite to a third molecule of the hypochlorite which is oxidised to chlorate. Lunge's experiments show that the best mode of converting hypochlorite into chlorate is to raise the temperature of the solution, slight excess chlorine being at the same time present. The heat produced by the reaction on the large scale is sufficient.

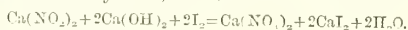
Pure calcium chlorate is prepared by precipitating potassium chlorate with calcium silicofluoride. It crystallises in deliquescent rhomboidal plates, very soluble in water and alcohol; the crystals contain 16.5 p.c. water, melt when warmed, and decompose on further heating.

**Calcium perchlorate**  $\text{Ca}(\text{ClO}_4)_2$  may be obtained by saturating perchloric acid with caustic lime. It is extremely deliquescent and crystallises in prisms soluble in alcohol.

**Calcium bromide**  $\text{CaBr}_2$  is formed by burning calcium in bromine vapour, or by dissolving lime or calcium carbonate in hydrobromic acid and evaporating. The silky needles thus obtained are hydrated, but may be converted to the anhydrous salt by ignition. Calcium bromide much resembles the chloride in properties, being deliquescent, and very soluble in alcohol.

**Calcium iodide**  $\text{CaI}_2$  may also be prepared by combustion of calcium in iodine vapour, or by solution of lime or the carbonate in hydriodic acid, evaporating and fusing the residue in a closed vessel. Heated in contact with air, it fuses below a red heat, and is decomposed with liberation of iodine vapours and formation of lime. The following methods of preparing it are recommended by Wagner (C. C. 1863, 143; J. 1862, 132):—

(1) Addition of iodine to an aqueous pulp of calcium sulphite and hydrate. (2) Addition of iodine, to saturation, to calcium thiosulphate stirred up with water, whereby a mixture of iodide and tetrathionate is formed, which may be used for technical purposes instead of potassium iodide. (3) Addition of iodine, finely divided or dissolved in potassium iodide, to calcium nitrite and hydrate, thus:



And (4) addition of finely divided iodine to a concentrated mixture of arsenious oxide and milk of lime; insoluble arsenate and soluble iodide of calcium are formed. The  $\text{As}_2\text{O}_3$  may be replaced by  $\text{Sb}_2\text{O}_3$ .

Liebig (A. 121, 222) recommends decomposition of  $\text{CaI}_2$  by  $\text{K}_2\text{SO}_4$  for preparation of iodide of potassium. To prepare the calcium iodide, 1 oz. of amorphous phosphorus is drenched



with 30 oz. hot water, and finely pulverised iodine gradually added, with constant stirring as long as it dissolves without colour (quantity thus dissolved being  $13\frac{1}{2}$  oz.). The colourless liquid is then decanted from the slight deposit, and made slightly alkaline with milk of lime (8 oz. lime being required); the solution is afterwards strained, and residue of phosphate, phosphite, and hydrate of calcium washed. The solution then contains the calcium iodide which may, if necessary, be obtained by evaporation in the form of hydrate in deliquescent needles.

A double iodide of calcium and silver of the composition  $\text{CaI}_2 \cdot 2\text{AgI} \cdot 6\text{H}_2\text{O}$  has been prepared by Simpson (Pr. 27, 120) by saturating a hot concentrated solution of  $\text{CaI}_2$  with moist silver iodide. It crystallises on cooling in long white needles, decomposed by water.

Calcium iodate  $\text{Ca}(\text{IO}_3)_2$  is obtained by crystallising mixed solutions of potassium iodate and calcium chloride. The hydrated salt forms four-sided prisms which effloresce in the air, and become anhydrous when heated to  $200^\circ$ . From a solution acidulated with nitric acid it separates in trietric crystals. The crystals are soluble in 454 parts water at  $18^\circ$ , and in 102 parts of boiling water, but are insoluble in alcohol. The anhydrous salt, gently heated in a porcelain retort, evolves  $14\cdot78$  p.c. of oxygen, and  $54\cdot07$  of iodine, leaving  $31\cdot14$  p.c. of a residue rich in pentabasic periodate of calcium. Heated more strongly it evolves more oxygen and iodine, and leaves  $20\cdot35$  p.c. of a mixture of pentabasic periodate and free lime. Calcium iodate detonates violently when heated on charcoal.

Sonstadt proposes (Pat. 6,304, 1884) to use calcium iodate as an antiseptic.

**Periodates of calcium.** When the sodium salt  $\text{NaH}_2\text{IO}_6$  is decomposed by calcium nitrate a crystalline white precipitate of dicalcium periodate  $\text{CaH}_2\text{IO}_6$  or  $2\text{CaO} \cdot 3\text{H}_2\text{O} \cdot \text{I}_2\text{O}_5$  is obtained. When this salt is heated, water, oxygen, and iodine are given off and pentacalcium periodate  $\text{Ca}_5\text{I}_2\text{O}_{12}$  remains (Langlois).

**Calcium fluoride**  $\text{CaF}_2$  is found in nature as *fluor-spar*, both in massive and crystallised forms; the crystals generally consist of octahedra, cubes, or other forms of the cubic system. Fluor-spar occurs generally in veins, especially in the celebrated Castleton district of Derbyshire, where it is known by the name of 'Blue John.' Pure crystals are colourless, but many varieties are coloured blue, violet, red, or yellow. It is also a constituent in small quantities of many plant ashes, of bones, and of the enamel of teeth. When precipitated calcium fluoride, obtained by precipitating any soluble calcium salt with fluoride of sodium or potassium, is heated with water slightly acidified with hydrochloric acid, the precipitate is found to consist of microscopic octahedrons.

Calcium fluoride is soluble in about 2,000 parts of water at  $15^\circ\text{C}$ ., and is slightly more soluble in water containing carbon dioxide. It dissolves in hydrofluoric acid and in strong hydrochloric acid and is precipitated in the gelatinous form by ammonia. It is fusible at a high temperature, and is much used as a flux in many metallurgical operations, especially in the reduction of copper ores and the preparation of aluminium. It is decomposed at a high temperature by

water vapour into lime and hydrofluoric acid. Fusion with alkaline carbonates or hydrates yields carbonate or oxide of calcium and alkaline fluorides. Strong sulphuric acid, on gently warming, decomposes it, forming calcium sulphate and liberating hydrofluoric acid. At a red heat it is also decomposed by chlorine. After being heated fluor-spar phosphoresces in the dark. There is a considerable industry carried on in fluor-spar districts in the carving of ornamental vases and other articles, the brilliantly coloured varieties being especially in demand.

**Calcium carbonate**  $\text{CaCO}_3$  occurs naturally in the forms of limestone, chalk, marble, and calcite; it also constitutes the principal ingredient in egg-shells, mollusc shells, and coral. It is formed when the oxide or hydrate is exposed to moist air containing carbon dioxide, but is not produced by the action of dry carbon dioxide on dry lime. It may be obtained in the pure state by dissolving chalk or marble or calcined oyster shells in hydrochloric acid, precipitating the alumina, oxide of iron, and earthy phosphates by ammonia or milk of lime, filtering, then precipitating the calcium by ammonium carbonate, washing and drying.

Calcium carbonate is dimorphous, crystallising in the hexagonal system as calc spar and in the rhombic system as arragonite. Calc spar or calcite crystallises in hemihedral forms of the hexagonal system chiefly in rhombohedra or prisms terminated by rhombohedral faces. The primary form is a rhombohedron having angles of  $101^\circ 5'$  and  $71^\circ 5'$ . Its sp.gr. is  $2\cdot7$  to  $2\cdot75$ . When a calcium salt is precipitated by an alkaline carbonate, the precipitate at first is flocculent, but soon takes the crystalline form of calcite. That formed by passing a small quantity of carbon dioxide through lime-water soon takes the crystalline form of calc spar, but if the solution be hot the crystals resemble those of arragonite. Calcite crystals are deposited from a solution of calcium carbonate in carbonic acid when evaporated at the ordinary temperature, but the crystals take the form of arragonite if the solution is heated to  $90^\circ$ . The microscopic crystals of arragonite gradually change into rhombohedra of calcite, which is therefore the permanent form. Arragonite crystallises in rhombic prisms of sp.gr.  $2\cdot92$ – $3\cdot28$ .

A litre of water dissolves about 18 milligrams of calcium carbonate. The solution has a slight alkaline reaction. Water containing carbonic acid dissolves it much more readily, forming the acid carbonate  $\text{CaH}(\text{CO}_3)_2$ , which is known only in solution. Solubility at higher pressures in water containing carbonic acid follows the law of Schloesing pretty closely (Engel, C. R. 101, 949). The solubility increases under an increase of pressure only up to 3 grams per litre according to Caro. One litre of water saturated with carbon dioxide dissolves  $0\cdot7$  gram of the carbonate at  $0^\circ$ , but  $0\cdot88$  gram at  $10^\circ$ . This acid carbonate plays a most important part in nature, for whenever water containing carbonic acid comes in contact with carbonate or silicates of calcium, the calcium is gradually converted into this soluble form and is therefore found in almost all natural waters. Hence also the deposits in kettles and boilers; the formation of

which may be prevented by the addition of ammonium chloride to the water.

Calcium carbonate, when heated to full redness in open vessels, is decomposed into lime and carbon dioxide. The decomposition commences at a low red heat, and in a current of air, or better steam, the temperature of dissociation is lower still. The tension of dissociation becomes equal to the pressure of the atmosphere, according to Le Chatelier (C. R. 102, 1,243) at about  $812^{\circ}$ . If heated rapidly, the stationary temperature of dissociation is  $925^{\circ}$ . At  $547^{\circ}$  the tension of dissociation is 27 mm.; at  $610^{\circ}$ , 46 mm.; at  $625^{\circ}$ , 56 mm.; at  $740^{\circ}$ , 245 mm.; at  $810^{\circ}$ , 678 mm., and at  $865^{\circ}$ , 1,333 mm. If the carbonate be ignited in a closed vessel it fuses, resolidifying to a mass of marble-like calcite. According to Becker (J. M. 1886, 1, Ref. 403) any form of  $\text{CaCO}_3$ , even at a low pressure, is changed on heating in a closed space with exclusion of air into the rhombohedral form without fusion. If small quantities of the precipitated carbonate are thrown into a fused mixture of sodium and potassium chlorides in equivalent proportions, no carbon dioxide is evolved, but the carbonate becomes crystalline calcite, usually in aggregations of crystals like snow crystals (Bourgeois, Bl. [2], 37, 447).

#### Pentahydrated calcium carbonate $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ .

The evaporation of natural solutions of the acid carbonate generally results in the deposition of the ordinary carbonate, forming the stalactites and stalagmites of caverns, calcareous tufas, and other forms of deposit; but sometimes the solution yields six-sided rhombic prisms of the composition  $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ . These crystals are often found in pumps and pipes leading from wells, also adhering to the confervæ in ponds. They keep unaltered under water at  $20^{\circ}$ , but at slightly higher temperatures lose their transparency and water of crystallisation. In air they crumble to powder through loss of water (Pfeiffer, Ar. Ph. [2] 15, 212). This salt, according to Pelouze (A. Ch. [2] 48, 301) is obtained in small acute rhombohedra, sp.gr. 1.783, by boiling lime in a concentrated solution of sugar, starch, or gum, and leaving the solution for some months in a cold place. Becquerel, by exposing a solution of lime in sugar water to a voltaic battery of twelve cells, obtained crystals of the same composition, but in form of rhombic prisms.

**Basic carbonates of lime.** Calcium oxide commences to absorb carbon dioxide at a temperature of  $415^{\circ}$ , forming a basic carbonate of the composition  $2\text{CaO} \cdot \text{CO}_2$  (Birnbaum and Mahu, B. 12, 1,547).

Raoult (C. R. 92, 1,457) shows that when freshly burnt lime is heated in a current of carbon dioxide it glows strongly, forming  $2\text{CaO} \cdot \text{CO}_2$  which does not disintegrate in moist air and does not take up water from steam at  $200^{\circ}$ . When finely powdered and treated with a little water it hardens like hydraulic cement. The hydrated product has the composition  $\text{CaCO}_3 \cdot \text{Ca}(\text{OH})_2$ . On heating to dull redness it loses water and is converted into a mixture of  $\text{CaCO}_3$  and  $\text{CaO}$ .

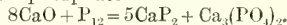
When burnt lime is heated in contact with carbon dioxide for several days the basic salt

$2\text{CaCO}_3 \cdot \text{CaO}$  is obtained, which still absorbs  $\text{CO}_2$  forming a third salt  $3\text{CaCO}_3 \cdot \text{CaO}$ . The carbon dioxide continues to be absorbed, however, and appears eventually to form the normal carbonate.

**Calcium nitrite**  $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$  is prepared by decomposing a boiling solution of silver nitrite with lime-water, treating the filtrate with sulphuretted hydrogen and carbonic acid to remove excess of silver and calcium, and evaporating at a gentle heat. It crystallises in deliquescent prisms insoluble in alcohol.

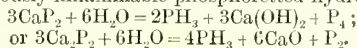
**Calcium nitrate**  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  occurs as a silky efflorescence in limestone caverns, especially those of Kentucky, also on the walls of places where there is much organic refuse. It is found in many well waters, being derived from the soil. It is extremely deliquescent and soluble, and causes rapid disintegration of mortar, and hence is called 'saltpetre rot.' It may be prepared by dissolving the carbonate in nitric acid, the solution depositing on slow evaporation monoclinic six-sided prisms terminated by acute pyramids of the above composition. On evaporating the solution to dryness the anhydrous salt of sp.gr. 2.472 is obtained, possessing a warm bitter taste and readily soluble in water and alcohol. On heating more strongly it becomes phosphorescent, as noticed by Baldwin in 1674, and hence is termed *Baldwin's phosphorus*. At a higher temperature oxygen and nitric peroxide are evolved, and with combustible bodies detonation occurs. It is extensively prepared on the Continent for the manufacture of nitre by mixing vegetable and animal refuse with chalk, marl, cinders, &c., moistening from time to time with liquid stable manure, and exposing to the air for two or three years, when the mass is lixiviated and the crude nitrate of calcium decomposed by carbonate, sulphate, or chloride of potassium.

**Calcium phosphide.** When metallic calcium is heated with phosphorus under petroleum combination occurs. Calcium phosphide mixed with pyrophosphate is also obtained when vapour of phosphorus is passed over red-hot lime:  $14\text{CaO} + 14\text{P} = 5\text{Ca}_3\text{P}_2 + 2\text{Ca}_4\text{P}_3\text{O}_{10}$ . A few pieces of phosphorus are placed at the closed end of a combustion tube, and the tube is filled with small pieces of quick-lime, and the lime is heated to redness and the heat gradually extended to the phosphorus. The phosphide may be prepared on a larger scale by filling a crucible with a hole in its base with pellets of lime, and placing it upon the grate of a furnace. A flask containing phosphorus is placed below the grating with its neck passing into the hole of the crucible. When the lime has been heated to redness the phosphorus is gradually heated so that its vapour passes through the lime. The brown mass is stated by Gmelin (Handb. 3, 188) to be a mixture of monocalcium phosphide and tricalcium phosphate:

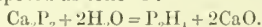


It may be that both this and the former reaction are correct and that both mono- and di-phosphides are formed.

When thrown into water the product is instantly decomposed with evolution of spontaneously inflammable phosphoretted hydrogen



Possibly some of the diphosphide may also be decomposed as follows :



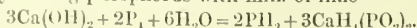
In this way the spontaneous inflammability of the phosphoretted hydrogen would be accounted for.

Owing to this property calcium phosphide is utilised for the production of signal fires at sea. The manufacture is carried on in an arrangement similar to the above, the crucibles being larger and divided by a false perforated bottom into two compartments, in the upper of which the pieces of lime are raised to a red heat, the phosphorus placed in the lower compartment being afterwards volatilised by the heat radiated from above. In about six hours a charge yielding 20 lbs. of product is finished. The brown stony mass is immediately worked up into the 'lights.' These consist of cylindrical tinned-iron boxes, the lower half of which is filled with about 16 oz. of the fragments of phosphide. Two small circular portions of the upper and under surfaces of metal are formed of soft lead, so that they may be pierced by a knife just before being thrown overboard. The tins are supported by a wooden float when in use. The water enters below and the gas issues from the upper outlet, burning with a flame 9 to 18 inches high lasting about half an hour. Larger but similar 'lights' are prepared to be placed in a bucket of water on deck. In the British navy torpedo practice, a peculiar form of the phosphide is also used.

**Calcium phosphite**  $\text{CaHPO}_3 \cdot \text{H}_2\text{O}$  separates as a crystalline crust from a solution of the ammonium salt mixed with calcium chloride. It is sparingly soluble in cold water, and the solution decomposes when heated, depositing a basic salt, an acid salt remaining dissolved. It gives off its water at  $100^\circ$ . According to Rother (Ph. [3], 10, 286), when solutions of calcium hypophosphite and sodium sulphite are mixed, calcium sulphite is precipitated; if this is re-dissolved in enough hydrochloric acid to free all the hypophosphorous and sulphurous acids and the sulphur filtered off, on addition of ammonia a crystalline precipitate of calcium phosphite separates. It is a white crystalline powder, which, on heating, evolves spontaneously inflammable phosphoretted hydrogen, accompanied by slight detonations. At a certain temperature it becomes incandescent, and leaves a residue of calcium phosphate.

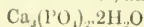
An acid phosphite  $\text{CaH}_2(\text{PO}_3)_2 \cdot \text{H}_2\text{O}$  is obtained as a crystalline crust by acting upon marble with aqueous phosphorous acid as long as carbon dioxide escapes. The crust consists of needle-shaped crystals soluble in water, and losing their water at  $100^\circ$ .

**Calcium hypophosphite**  $\text{Ca}(\text{PO}_2)_2$  or  $\text{CaH}_2(\text{PO}_2)_2$  is used medicinally, and is prepared by boiling phosphorus with milk of lime

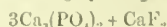


On evaporation the hypophosphite is obtained in monoclinic flexible prisms insoluble in alcohol. When heated it evolves phosphoretted hydrogen and water, leaving calcium pyrophosphate.

**Calcium orthophosphate**  $\text{Ca}_3(\text{PO}_4)_2$  occurs pure in the mineral *osteolite*, and as



in *ornithite*. Together with calcium fluoride or chloride, it occurs largely in *apatite*



and in the massive varieties *phosphorite* and *estramadurite* found in Estramadura, in Spain, where it forms vein-like layers in the granite of the palaeozoic slates and Devonian limestones. In certain apatites the  $\text{CaF}_2$  is more or less replaced by  $\text{CaCl}_2$ .

Calcium phosphate also forms a principal constituent of the coprolites frequently found in the stratified rocks. It is the chief inorganic material of bones, forming about 80 p.c. of burnt bones.

It is obtained in the amorphous state by precipitating an ammoniacal solution of calcium chloride with excess of hydrogen disodium phosphate. The precipitate is gelatinous, but dries up to a white earthy powder, nearly insoluble in water, but is decomposed by long boiling into an insoluble basic salt of the composition

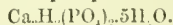


and a soluble acid salt. This reaction also occurs slowly in the cold. Calcium phosphate is also soluble in water containing carbonic acid, ammonium salts, nitrate of soda, sodium chloride and other salts. Its absorption by the roots of plants is therefore promoted by the agency of saline solutions.

Calcium orthophosphate may be obtained in the crystalline form by heating dicalcium pyrophosphate with water, whereby it is resolved into phosphoric acid and tricalcium phosphate which separates in rectangular plates  $3\text{Ca}_2\text{P}_2\text{O}_7 + 3\text{H}_2\text{O} = 2\text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_3\text{PO}_4$ .

Tricalcium phosphate is not decomposed by ignition.

#### Dicalcium orthophosphate



An aqueous solution of phosphoric acid acts on precipitated chalk forming small needle-shaped crystals of dicalcium phosphate, and the finely divided chalk deposited from marls in the beds of streams is particularly suitable for its preparation by this method (Ritthausen, L. V. 20, 401). Dried at  $100^\circ$  the salt contains  $5\text{H}_2\text{O}$  which it does not lose below  $115^\circ$ . It is soluble in ammonium citrate. Boiled with water it is partially decomposed into tricalcium phosphate.

On mixing boiling solutions of sodium phosphate, calcium chloride and acetic acid



is formed; if the solutions are mixed in the cold  $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$  is formed (Millot, Bl. [2] 33, 194).

When a solution of calcium chloride is mixed with one of ordinary sodium phosphate a white crystalline precipitate of  $\text{Ca}_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  is thrown down. It is this salt which is occasionally deposited from wine in stellar aggregates. According to Becquerel and Berzelius a trihydrate may also be obtained. These different results as regards water of crystallisation are probably owing to the fact that the precipitates vary in amount of water and solubility in acids according to the conditions of their precipitation.

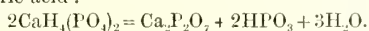
A manufacturing process is described by De Bouquet (B. C. 1884, 411) in which a solution of calcium sulphhydrate is run in fine jets



into a hydrochloric acid solution of a phosphate; sulphuretted hydrogen escapes and the diphosphate is precipitated. If the acid solution be treated with the sulphhydrate to alkaline reaction, the tricalcium phosphate is formed.

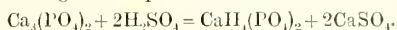
**Monocalcium phosphate**  $\text{CaH}_2(\text{PO}_3)_2$  is obtained in rhombic tables by dissolving either of the former phosphates in phosphoric acid and allowing the solution to spontaneously evaporate. It has a strong acid reaction, and deliquesces in air, dissolving readily in water. A small quantity of water decomposes it, forming insoluble dicalcium phosphate and free phosphoric acid. If cold, the hydrate  $\text{Ca}_2\text{H}_2(\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$  is formed; if hot, the same salt, free from water, is precipitated.

Monocalcium phosphate fuses on heating, giving up its water, and when heated to  $200^\circ$  it parts with the elements of water, leaving a mixture of calcium pyrophosphate and metaphosphoric acid:



When the mixture is heated to a still higher temperature, pure calcium metaphosphate remains.

**Superphosphate of lime** is a mixture of monocalcium phosphate and calcium sulphate which is manufactured as a manure. It is prepared by acting on bone-ash, coprolites, phosphorites, or other mineral phosphates with two-thirds their weight of sulphuric acid:



Besides its use as a manure for root-crops, it is used in the manufacture of phosphorus.

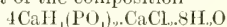
**Calcium pyrophosphate**  $\text{Ca}_2\text{P}_2\text{O}_7$  is prepared by action of aqueous pyrophosphoric acid upon lime-water, or sodium pyrophosphate upon calcium chloride. If the precipitate thus obtained is dissolved in sulphurous acid and the solution heated, the salt separates as a crystalline crust. The crystals contain four molecules of water.

**Calcium metaphosphates.** The monosalt  $\text{Ca}(\text{PO}_3)_2$  is obtained by dissolving calcium carbonate in orthophosphoric acid, evaporating and heating the residue to  $316^\circ$ . It is an insoluble white powder.

The di-metaphosphate  $\text{Ca}_2(\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$  is obtained pure in the crystalline form by precipitating the corresponding alkali salt with excess of calcium chloride. It is insoluble in water, but is decomposed by strong sulphuric acid. A double dimetaphosphate of calcium and ammonium  $\text{Ca}(\text{NH}_4)_2(\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$  is obtained in spicular crystals by mixing a solution of calcium chloride with excess of the ammonium salt. It is insoluble in water.

**Phosphato-chlorides of calcium** are obtained by evaporating solutions of tricalcium phosphate in hydrochloric acid. A saturated solution, on spontaneous evaporation, deposits rhomboidal plates of  $7\text{CaH}_2(\text{PO}_3)_2 \cdot \text{CaCl}_2 \cdot 14\text{H}_2\text{O}$ . If the solution is evaporated over the water-bath, dicalcium phosphate is first deposited, then, on further evaporation, the above phosphatic chloride comes down, and afterwards white scales of  $\text{CaH}_2(\text{PO}_3)_2 \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$ . When a solution of dicalcium orthophosphate in hydrochloric acid is saturated at ordinary temperatures with tricalcium phosphate, then mixed with half the quantity of hydrochloric acid already contained

in it, and evaporated, on cooling below  $6^\circ$  crystals separate out of the composition

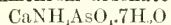


(Erlenmeyer, J. 1857, 146).

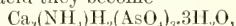
**Calcium silico-phosphate.** According to Carnot and Richard (C. R. 97, 316), the brownish-black slag formed in working the Thomas-Gilchrist process at Jœuf (Meurthe-et-Moselle) is covered with black crystals, some slender needles, others right rhombic prisms with brilliant faces, frequently aggregated in columnar masses terminating in vitreous, translucent, blue crystals. Similar blue crystals are found in the cavities, possessing the constant composition  $8\text{P}_2\text{O}_5 \cdot 8\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{FeO} \cdot 36\text{CaO}$ , essentially a calcium silico-phosphate  $\text{Ca}_3(\text{PO}_3)_2 + \text{Ca}_2\text{SiO}_4$ .

**Calcium arsenates.** Dicalcium arsenate occurs native as *haidingerite*  $\text{Ca}_2\text{H}_2(\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$ , and *pharmacolite*  $\text{Ca}_2\text{H}_2(\text{AsO}_4)_2 \cdot 5\text{H}_2\text{O}$ , and may be prepared by adding a solution of disodium arsenate to excess of calcium chloride. The tetrahydric arsenate obtained by addition of lime-water to arsenic acid is soluble, while the tricalcium arsenate is insoluble in water, and may be prepared by precipitating calcium chloride with trisodium arsenate. On evaporating a hydrochloric acid solution of calcium ammonium arsenate with platinum chloride, the mass left on ignition of the platinochloride is found to contain fine white prisms of the tricalcium orthoarsenate  $\text{Ca}_3(\text{AsO}_4)_2$  insoluble in acids. The meta-arsenate  $\text{Ca}(\text{AsO}_3)_2$  is formed as an insoluble crystalline powder when mixtures of arsenious anhydride and calcium carbonate are ignited.

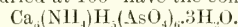
#### Calcium ammonium arsenate



is produced by mixing a hot solution of arsenic acid in excess of ammonia with calcium nitrate or chloride, when it crystallises on cooling in tables arranged like steps. In a vacuum over sulphuric acid they become



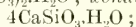
and when dried at  $100^\circ$  have the composition



On ignition they are converted into calcium pyroarsenate  $\text{Ca}_2\text{As}_2\text{O}_7$  (Bloxam, C. N. 54, 168).

Another salt,  $\text{Ca}(\text{NH}_4)_2\text{H}_2(\text{AsO}_4)_3$ , is obtained by adding excess of ammonia to a solution of dicalcium arsenate in nitric acid, as a flocculent precipitate, soon becoming a mass of needles. The same salt is obtained in crystals belonging to the regular system when the solution of the dicalcium salt is only partially precipitated and allowed to stand; hence it appears to be dimorphous (Baumann).

**Calcium silicates.** Calcium oxide is an important base in a large number of natural silicates, and is the principal basic constituent of the following minerals: *Wollastonite*  $\text{CaSiO}_3$ , or tabular spar, occurring in monoclinic crystals; *okenite*  $\text{CaH}_2(\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$ ; *xonallite*



*gurolite*  $\text{Ca}_2\text{H}_2(\text{SiO}_3)_3 \cdot \text{H}_2\text{O}$ ; and *apophyllite*,  $4\text{CaH}_2(\text{SiO}_3)_2 \cdot \text{KF} \cdot 4\text{H}_2\text{O}$ .

Gorgeu (C. R. 99, 256) obtained artificial wollastonite by fusing 1 gram of silica with 15 grams calcium chloride and 3 grams common salt at a cherry-red heat in a current of moist air for half an hour. On treating the product with cold water and acetic acid, a residue of

long prisms of wollastonite mixed with round grains of tridymite was obtained. The artificial wollastonite possessed the same chemical and optical properties and crystalline form as the natural, but was somewhat softer, the hardness of the mineral being 5, and that of the artificial 3·5.

If molecular proportions of precipitated silica and calcium chloride are heated to a high temperature in presence of water vapour,  $\text{CaSiO}_3$  is also formed, but not in form of wollastonite. With twice the amount of chloride the normal silicate  $\text{Ca}_2\text{SiO}_4$  is formed.

Doelter (J. M. 1886, 1, 119) found that in absence of steam a hexagonal  $\text{CaSiO}_3$  is always formed; hence wollastonite must have been formed in presence of steam. Calcium silicate is therefore dimorphous.

The silicates  $2\text{CaO}.\text{SiO}_2$ ,  $2\text{CaO}.3\text{SiO}_2$ ,  $\text{CaO}.2\text{SiO}_2$ , and  $\text{CaO}.3\text{SiO}_2$  are produced by exposing mixtures of quartz and marble in these proportions to the heat of a smith's forge. The last three are the most fusible.

On precipitating the solution of any calcium salt with sodium or potassium silicate, the silicates  $2\text{CaO}.9\text{SiO}_2.3\text{H}_2\text{O}$  and  $\text{CaO}.\text{SiO}_2$  have been obtained by Lefort and Von Ammon respectively.

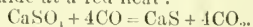
Gorgeu (C. R. 99, 256) obtained two chlorosilicates by heating to a high temperature silica and calcium chloride in proportion of one molecule to seven in presence of water vapour. The first,  $2\text{CaO}.\text{SiO}_2.\text{CaCl}_2$ , forms birefractive rhombic plates. The second,  $\text{CaO}.\text{SiO}_2.\text{CaCl}_2$ , forms hexagonal plates, and is produced more rapidly than the former, which requires prolonged heating. Both compounds are decomposed by water.

**Calcium silico-borate**  $\text{CaO}.2\text{SiO}_2.\text{CaB}_2\text{O}_4$  occurs with one molecule of water as *datholite*, and with two molecules of water as *botryolite*.

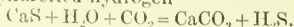
**Calcium silico-titanate**  $\text{CaO}.3\text{SiO}_2.2\text{CaTiO}_3$  occurs as *sphene*.

**Calcium monosulphide**  $\text{CaS}$ . Perfectly dry lime remains unaltered on passing over it a current of dry sulphuretted hydrogen; but on hydrating the lime and again passing the gas, calcium sulphide is formed:  $\text{Ca}(\text{OH})_2 + \text{H}_2\text{S} = \text{CaS} + 2\text{H}_2\text{O}$ . The most favourable temperature is  $60^\circ$  (Velej, C. J. 1885, 478).

It may also be prepared by heating the sulphate with coal or charcoal, or by action of carbonic oxide at a red heat:



Anhydrous calcium sulphide is a white powder which emits a smell of  $\text{SH}_2$  in the air. It turns yellow on moistening, due to the formation of oxidised products. It is but sparingly soluble in water, and is decomposed by boiling water, with formation of hydrate and sulphhydrate of calcium  $2\text{CaS} + 2\text{H}_2\text{O} = \text{Ca}(\text{HS})_2 + \text{Ca}(\text{HO})_2$ . Suspended in water it is readily decomposed by carbonic acid, with formation of calcium carbonate and sulphuretted hydrogen



After being heated, calcium sulphide shines in the dark, and was long known as Canton's phosphorus.

According to Verneuil (C. R. 103, 600), calcium sulphide with a violet phosphorescence may be prepared as follows: 20 grams of finely-

powdered lime, obtained by heating the shells of *Hyppopus vulgaris*, is intimately mixed with 6 grams of sulphur and 2 grams of starch, and 8 c.c. of a solution containing 0·5 gram basic bismuth nitrate and 100 c.c. of absolute alcohol acidified with a few drops of hydrochloric acid are added. The mixture is exposed to the air until most of the alcohol has evaporated, and is then heated to cherry redness for twenty minutes. When completely cooled, the upper layer of calcium sulphate is removed, and the calcined mass powdered and again heated fifteen minutes. The violet phosphorescence of the product is due to the trace of bismuth. 0·1 p.c. of sulphides of antimony, cadmium, mercury, tin, copper, lead, uranium, platinum, or zinc imparts a bluish or yellowish-green tint to the phosphorescence. Manganese produces an orange shade. A mixture of 100 parts lime, 30 parts sulphur, 10 of starch, and 0·035 of lead acetate yields a sulphide with a beautiful yellowish-green phosphorescence.

Pure calcium carbonate mixed with 2 p.c. sodium carbonate and 0·02 p.c. of common salt, heated with 30 p.c. sulphur and 0·02 p.c. bismuth nitrate, yields a similar product to that obtained by use of *Hyppopus* shells. Pure calcium sulphide does not phosphoresce; the phenomenon is due to small quantities of impurities; thus in the last mixture it has been shown by Verneuil to be due to simultaneous presence of traces of bismuth oxide, sodium carbonate and chloride and calcium sulphate.

These phosphorescing varieties of calcium sulphide are utilised in the manufacture of luminous paints. Abney (P. M. [5] 13, 212) found that the emission spectrum showed greatest luminosity between G and F, and a feeble one extending from between E and F as far as the red. The rays of the electric light somewhat beyond H on one side and G on the other are most active in exciting phosphorescence.

**Calcium disulphide**  $\text{CaS}_2$  is deposited in yellow crystals of the composition  $\text{CaS}_2.3\text{H}_2\text{O}$  from the solution obtained by boiling sulphur with milk of lime and filtering whilst hot.

**Calcium pentasulphide**  $\text{CaS}_5$  is formed when the monosulphide or hydrate of calcium is boiled for a long time with excess of sulphur. Concentrated solutions of calcium hydrosulphide  $\text{Ca}(\text{HS})_2$  also react energetically upon powdered roll sulphur, on preventing access of air by performing the operation in a current of hydrogen; an orange-red solution is produced with fall of temperature, and on warming the calcium is completely converted into  $\text{CaS}_5$ . The reaction is reversible, a current of sulphuretted hydrogen causing deposition of sulphur and re-formation of hydrosulphide.

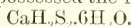
**Calcium oxysulphides**. When hydrate of calcium is used as above, besides  $\text{CaS}_5$ , there is also formed an oxysulphide of the composition  $5\text{CaS}.\text{CaO}.20\text{H}_2\text{O}$  (Rose). The same substance is obtained in gold-coloured needles when the solution obtained by boiling crude calcium monosulphide with much water is evaporated.

According to Hoffmann (C. R. 62, 291) a mixture of two molecules of calcium monosulphide and one molecule lime at a red heat forms the oxysulphide  $2\text{CaS}.\text{CaO}$ . This oxysulphide is contained in recently lixiviated soda residues.

Genther (A. 224, 178) obtained crystals of  $\text{CaS}_2 \cdot 2\text{CaO} \cdot 10\text{H}_2\text{O}$  by boiling sulphur in milk of lime. They dissolve in hydrochloric acid forming hydrogen persulphide  $\text{H}_2\text{S}_2$  and a little  $\text{H}_2\text{S}$ . On boiling calcium monosulphide and sulphur with water crystals of  $\text{CaS}_2 \cdot 3\text{CaO} \cdot 15\text{H}_2\text{O}$  were obtained. Divers obtained a compound of the formula  $11\text{CaS} \cdot 5\text{CaO}$  by igniting lime in a mixture of carbon dioxide and carbon bisulphide.

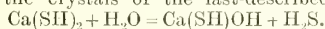
**Calcium sulphhydrate**  $\text{Ca}(\text{HS})_2$  is formed together with the hydrate when the monosulphide is boiled with water. The best mode of preparing it is to pass sulphuretted hydrogen through the hydrate or sulphide suspended in water, with constant agitation, until it ceases to be absorbed. It is difficult to obtain in the solid state, being decomposed when the stage of crystallisation is reached into  $\text{SH}_2$  and  $\text{CaS}$  which separates in silky prisms.

Divers (C. J. 1884, 270) obtained it in the solid form by forcing sulphuretted hydrogen through semi-solid calcium hydrate and water so as to obtain a saturated solution of the sulphhydrate. Air was excluded, and on settling, decanting in a stream of  $\text{H}_2\text{S}$ , and cooling by ice, crystals formed in abundance. They were colourless prisms, melting on slight rise of temperature with partial decomposition. They readily dissolved in a fourth of their weight of water, and could not be removed from the atmosphere of sulphuretted hydrogen without decomposition. They possessed the formula



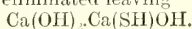
Calcium sulphhydrate may be used as a depilatory. If sulphuretted hydrogen be passed into thin milk of lime till the mass acquires a bluish-grey colour, the paste thus formed, when thinly laid upon the surface from which the hair is to be removed, permits of the ready removal of the hair a minute or two afterwards by scraping with a dull knife. It has been proposed to employ it in the tan-yard.

**Calcium hydroxy-sulphhydrate**  $\text{Ca}(\text{SH})(\text{OH})$  is formed according to Divers by action of water upon the crystals of the last-described salt:

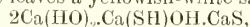


Also by union of water with calcium sulphide, as in interior of heaps of soda-waste; and by reaction between  $\text{Ca}(\text{OH})_2 + \text{H}_2\text{S}$  in the coal-gas purifier. Exposed to air crystals of  $\text{Ca}(\text{HS})_2$  are rapidly converted to  $\text{Ca}(\text{SH})(\text{OH})$ , and concentrated solutions of the sulphhydrate exposed to air become rapidly covered with crystals, and an abundant crop of crystals of  $\text{Ca}(\text{SH})(\text{OH})$  is obtained on passing in a current of air. The crystals are colourless four-sided prisms of silky lustre, easily obtained dry, of the composition  $\text{Ca}(\text{SH})(\text{OH}) \cdot 3\text{H}_2\text{O}$ . They slowly evolve  $\text{SH}_2$  in air and become yellow by absorption of oxygen. They are readily soluble in water, but the solution rapidly decomposes into hydrate and sulphhydrate. They are insoluble in alcohol.

According to Folkard (C. N. 49, 258) by exposing calcium hydrate to the action of sulphuretted hydrogen until it ceases to gain weight a grey powder of the composition  $4\text{Ca}(\text{HO})_2 \cdot 3\text{H}_2\text{S}$  is obtained. By the action of coal gas sulphuretted hydrogen is evolved from it, and at  $100^\circ$  water is eliminated leaving



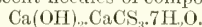
This greyish-green powder when gently heated in coal gas leaves a yellowish-white salt



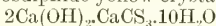
and this at a red heat forms  $2\text{CaO} \cdot \text{Ca}(\text{SH})(\text{OH}) \cdot \text{CaS}$  which when ignited in air burns like tinder to  $\text{CaSO}_4$ .

**Calcium sulpho-carbonate**  $\text{CaCS}_3$ . Lime over which coal gas containing sulphuretted hydrogen has been passed readily absorbs carbon bisulphide. Absorption is most complete when the lime is moistened with water; this material when fouled is mixed with an equal weight of slaked lime. The absorption of carbon bisulphide stops when one third of the sulphide is converted to sulpho-carbonate  $\text{CaS} + \text{CS}_2 = \text{CaCS}_3$ . On exposing the product for a short time to the air, it is again rendered capable of removing carbon bisulphide.

On passing hydrogen saturated with vapour of carbon bisulphide into a mixture of calcium monosulphide and a little water, the liquid becomes red and *in vacuo* deposits red prismatic very deliquescent needles of composition

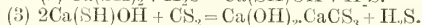
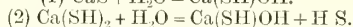
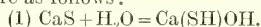


When the hydroxy-sulphhydrate is employed instead of monosulphide yellow crystals of



are obtained.

From these facts Veley (C. J. 1885, 478) concludes that the carbon bisulphide is absorbed by  $\text{Ca}(\text{SH})(\text{OH})$ , and not by  $\text{CaS}$ , and that the reactions are as follows:



The basic sulpho-carbonate is unstable, being decomposed slowly by sulphuretted hydrogen and readily by carbon dioxide.

When milk of lime is agitated with carbon bisulphide bright orange needles of a basic sulpho-carbonate  $\text{Ca}(\text{HO})_2 \cdot \text{CaCS}_3 \cdot 6\text{H}_2\text{O}$  are deposited.

**Calcium selenides.** The monoselenide is formed as a flesh-coloured precipitate by precipitating calcium chloride with potassium monoselenide. Lime-water saturated with seleniuretted hydrogen deposits crystals of calcium selenide when exposed to the air. When lime and selenium are heated just below redness a polyselenide mixed with calcium selenite is formed.

**Calcium sulphite**  $\text{CaSO}_3$  is formed when a solution of an alkaline sulphite is added to the solution of a calcium salt, as a white powder soluble in 800 parts of water. It dissolves in sulphurous acid, and the solution on exposure to air deposits six-sided needles of the composition  $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ .

The solution in sulphurous acid is known commercially as bisulphite of lime, and is manufactured by passing sulphur dioxide into milk of lime. In Kynaston's process (Pat. 15,659, 1884) a mixture of calcium chloride solution, magnesia, and a little carbonate of lime is brought into contact with sulphur dioxide. The  $\text{SO}_2$  is caused to ascend a flagstone tower packed with pigeon-holed brickwork, while the mixture is allowed to run down the tower in such proportions that from the base there runs a mixture of neutral sulphite of calcium suspended in a solution of magnesium chloride containing the excess



of sulphurous acid. The sulphite is settled out in tanks, the supernatant liquor drawn off and concentrated to 40-45° Tw.; then a quantity of alkali waste is added to it in a closed iron vessel, and the whole heated, when sulphuretted hydrogen is given off, and calcium chloride, magnesia, and calcium carbonate with alkali cinders remain. The latter are removed in a strainer and the emulsion is ready to be again treated with sulphur dioxide. The whole of the carbonate of lime present is converted to sulphite, carbon dioxide being evolved.

According to Birnbaum and Wittich (B. 13, 651), calcium oxide does not absorb sulphur dioxide gas below 400°, but at this temperature combination takes place rapidly with formation of a basic sulphite  $\text{Ca}_3\text{S}_2\text{O}_{16}$  or  $6\text{CaO} \cdot 5\text{SO}_2$ . At 500° the gas is rapidly absorbed, but the sulphite splits up into sulphate and sulphide.

Calcium sulphate  $\text{CaSO}_4$  is frequently found in limestone rocks or in company with common salt in the anhydrous state as the mineral *anhydrite*. Anhydrite occurs both in rhombic crystals and in a semi-crystalline massive form. More frequently the sulphate is found hydrated as *gypsum*  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , of which the well crystallised form is termed *selenite*, a fibrous variety *satinspar*, and a finely crystallo-granular form *alabaster*. Selenite occurs in fine monoclinic prisms, frequently twinned in characteristic arrow-head shapes.

The anhydrous sulphate may be artificially obtained in crystals resembling anhydrite of sp.gr. 2.9, by fusing calcium chloride with excess of potassium sulphate (Manross, J. 1852, 9).

Hydrated calcium sulphate is precipitated on adding dilute sulphuric acid or a soluble sulphate to an aqueous solution of calcium chloride. The specific gravity of gypsum is 2.31. When it is heated to 100-120° it gives up three-fourths of its water rather quickly, but it requires a temperature of 200-250° to expel the remainder. Dried at 100° the hydrate  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$  of sp.gr. 2.7 is left. The anhydrous salt fuses at a red heat without decomposition, and on cooling assumes the structure of anhydrite. When dehydrated calcium sulphate is pulverised and mixed with water it absorbs two molecules of water, and solidifies to a very hard mass with evolution of heat, expanding in so doing so as to fill any mould in which it is cast; hence the use of gypsum or plaster of Paris in preparing casts. If the gypsum has been heated to a little over 200°, thus being deprived of all its water, it becomes dead burnt and takes up water very slowly and without hardening.

Plaster of Paris is prepared very extensively on the large scale by burning gypsum. Its good qualities mainly depend upon the choice of raw material—heavier and denser varieties yielding the best commercial results—and upon the mode of burning. The lowest temperature at which gypsum can be advantageously burnt is 80°C., but a temperature of 110-120° gives the best technical results. As a rule also, the smaller the pieces the more homogeneous the product.

It is burnt in kilns or ovens, taking precautions not to permit the fuel to come in contact with it so as to reduce it to sulphide. The walls of the kilns are of strong masonry, spanned by a ventilated arch. The interior is divided into

two parts—an upper larger chamber for reception of the gypsum, and a lower series of small fire chambers beneath, where brushwood or coke is burnt to obtain the required temperature. In Seanegatty's oven the interior is divided by an arch about a foot from the floor, upon the under side of which play the flames from a furnace connected with the lower chamber, the hot air and gases passing afterwards through apertures into the gypsum chamber. The aqueous vapour passes away by a chimney at the top of the oven.

Dumesnil's oven is a form which has been much employed; it differs from Seanegatty's in the peculiar arrangement of the lower fire-room, which has twelve openings, the lower blocks of gypsum being arranged so as to facilitate the circulation of the draught from these. The firing is continued for about 4 hours, then the heat is increased for 8 hours, when all openings are closed, and 5-6 cubic metres of coarse gypsum powder spread equally over the top of the burning sulphate. By this means considerable saving of fuel is effected. After standing twelve hours to cool, the contents of the kiln are removed. It is mostly in state of powder, and the pulverisation is completed by grinding in a stamp or roller mill. The powder is then sifted and stored in a dry place.

Gradually these older types of furnaces are being replaced by continuous ones, of which those of Lecaze and Arson may be taken as types. The Lecaze furnace is rectangular, and consists of two chambers as before, but so arranged that the gypsum can be extracted at the base as fast as it is sufficiently dehydrated. The Arson furnace, one of the most successful, differs from all previous types in being charged with powdered gypsum. It consists of a cylindrical structure, divided into eight compartments by horizontal plates, perforated with circular holes. The gypsum is first powdered by means of a mill, from which it slides down an inclined plane to the mouth of the kiln, where it is distributed by automatic machinery upon the first horizontal plate, where it begins to be heated. After a time the distributor causes it to fall through the holes of this plate upon the second, where it is subjected to a still higher temperature, and so on through the whole eight. After passing through the eighth and lowest compartment, nearest the furnace, it is sufficiently dehydrated and falls as plaster of Paris into a receptacle common to a battery of ten similar furnaces. The fuel employed is coke, chosen so as to give no discolouring smoke. A battery of ten such furnaces dehydrates 100 cubic metres of gypsum in twenty-four hours.

Plaster of Paris can be hardened by mixture with a solution of alum. For further details of gypsum burning *v. CEMENTS*.

Calcium sulphate is very slightly soluble in water, the anhydrous sulphate being nearly insoluble. The solubility of the hydrate attains a maximum at 35°, one part dissolving in 393 parts water (Poggiale) at 0° in 488 parts, and at 100° in 460 parts. The solubility is increased by presence of hydrochloric or nitric acids, or chlorides of ammonium or sodium, hence its presence in salt springs; probably in most cases partial double decomposition has occurred

According to Lunge (S. C. I. 1885, 31) the solubility of calcium sulphate in solutions of sodium chloride increases with the percentage of salt but diminishes with increase of temperature.

At 21.5°C. 100 c.c. of a 3.53 p.c. solution of NaCl dissolves .5115 gram  $\text{CaSO}_4$ .

At 18.0°C. 100 c.c. of a 14.18 p.c. solution of NaCl dissolves .7340 gram  $\text{CaSO}_4$ .

At 101.0°C. 100 c.c. of a 3.53 p.c. solution of NaCl dissolves .4891 gram  $\text{CaSO}_4$ .

At 102.5°C. 100 c.c. of a 14.18 p.c. solution of NaCl dissolves .6248 gram  $\text{CaSO}_4$ .

Calcium chloride diminishes the solubility of  $\text{CaSO}_4$ , the more it is concentrated, but at the boiling-point the concentration is immaterial. Hydrochloric acid increases the solubility both with increase of concentration and of temperature.

Gypsum is readily soluble in excess of sodium thiosulphate, forming calcium thiosulphate, which combines with the excess of the sodium salt to form a soluble double thiosulphate. On addition of alcohol this double salt separates as a thick heavy liquid, which solidifies, forming needle-shaped crystals.

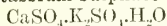
**Acid calcium sulphate**  $\text{CaSO}_4 \cdot \text{H}_2\text{SO}_4$  is formed by heating the neutral sulphate with strong sulphuric acid to 80–100°. A portion of the porous mass produced dissolves and separates on cooling in microscopic prisms of the composition above indicated. It is decomposed by water, even the moisture of the air, into gypsum and sulphuric acid.

**Calcium-sodium sulphate**  $\text{CaNa}_2(\text{SO}_4)_2$  occurs native in rhombic prisms as the mineral *glau-berite*. It may be obtained in the same form by fusing together calcium and sodium sulphates. On heating 50 parts sodium sulphate (Glauber's salt) with an emulsion of 1 part gypsum in 25 parts water to 80°, crystalline needles of

$\text{CaSO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  are deposited. On further heating these crystals are transformed into microscopic rhombohedral crystals of *glauberite*.

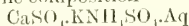
In the Welsh process of manufacturing sodium acetate, during evaporation of the liquor formed by double decomposition of calcium acetate by sodium sulphate, micaceous spangles of *glauberite* have been noticed by Folkard (C. N. 43, 6) to separate out. This explains why calcium sulphate so tenaciously retains sodium sulphate.

#### Calcium potassium sulphate



occurs native in monoclinic crystals as *syngenite*. It is formed by mixing solutions of the two salts. When a mixture of equal weights of anhydrous calcium sulphate and potassium sulphate is stirred up with less than its weight of water the mass suddenly solidifies. If 4.5 parts of water are used the solidification is not quite so rapid, but gives casts superior to those of plaster of Paris inasmuch as they possess a polished surface.

A salt of the composition



is obtained by adding an excess of potassium sulphate to a warm concentrated solution of ammonium sulphate which has been saturated with calcium sulphate. The same salt is formed when the double sulphate of calcium and po-

tassium is treated with a warm solution of ammonium sulphate (Fassbender, B. 11, 1, 968).

**Calcium thiosulphate**  $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  is prepared by heating an emulsion of calcium sulphate and sulphur in water.<sup>1</sup> It forms triclinic prisms soluble in their own weight of cold water. On heating the solution to 60° it is decomposed with deposition of sulphur. It is used for the preparation of antimony cinnabar  $\text{Sb}_2\text{OS}_3$ , used in oil painting.

**Calcium chromate**  $\text{CaCrO}_4 \cdot 4\text{H}_2\text{O}$  is prepared by dissolving calcium carbonate in aqueous chromic acid, or as a light-yellow precipitate on mixing concentrated solutions of chloride of calcium and potassium chromate. Bourgeois (J. M. 1880, 1 Ref. 351) prepares the anhydrous salt by heating to bright redness two molecules of the chloride with a molecule of potassium chromate and one of sodium carbonate. It forms slender yellow needles, formed from a rectangular prism, moderately soluble in water, and is used as a pigment. The hydrated salt gives up its water at 200°C.

The acid chromate  $\text{CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$  is obtained in red deliquescent crystals by evaporating a solution of the neutral salt in aqueous chromic acid.

**Calcium potassium chromate**  $(\text{CaK}_2)\text{CrO}_4 \cdot \text{Aq}$ . forms yellow silky needles, obtained by saturating acid chromate of potassium with calcium hydrate.

*Detection and estimation of calcium.*—The hydrated chloride when heated in a non-luminous flame on platinum wire imparts to the flame a red colour of less brilliancy than strontium, but still very distinct. If the compound to be tested is decomposed by hydrochloric acid, it is only necessary to moisten the platinum wire with the acid, and then dip it into the powdered substance. If the compound is a silicate, it should be powdered and mixed with ammonium fluoride, gently heating on platinum foil until the fluoride is volatilised; it is then moistened with sulphuric acid and tested in the flame on platinum wire, when the red colouration is obtained as soon as the excess of acid is driven off.

The spectrum of this red flame consists of a large number of lines, of which the green line  $\text{Ca}\beta$  is most prominent. Another characteristic line is the strong orange one  $\text{Ca}\alpha$ . A quantity of calcium chloride as little as  $\frac{1}{1000000}$  mgm. may be detected by the spectroscopic.

All the calcium salts except the sulphate dissolve readily in nitric or hydrochloric acid; the carbonate, phosphate, arsenate, and oxalate are insoluble, the sulphate sparingly, and almost all the other salts of calcium are readily soluble in water.

Ammonium carbonate precipitates calcium carbonate from solutions of calcium salts, thus separating it from the alkali-metals. In order to completely remove calcium (the carbonate being slightly soluble, 1 part dissolving in 40,000 parts water) it is usual to precipitate it by means of ammonium oxalate in ammoniacal solution, calcium oxalate being almost com-

<sup>1</sup> Divers (C. J. 1884, 279) obtains it by oxidation of calcium sulphhydrate in a current of air, calcium hydroxy-sulphhydrate being first formed and then oxidised by the  $\text{SH}_2$  to thiosulphate  $\text{Ca}(\text{SH})\text{OH} + 2\text{O}_2 + \text{H}_2\text{S} = \text{CaS}_2\text{O}_3 + 2\text{H}_2\text{O}$ .

pletely insoluble in water. It is distinguished from barium and strontium by the greater solubility of its sulphate, a solution of calcium sulphate giving an immediate precipitate with barium salts and one after some time with soluble strontium salts.

Calcium is generally estimated quantitatively as oxide or carbonate with intermediate precipitation as oxalate by addition of ammonia till the reaction is alkaline, and afterwards of ammonium oxalate. The washed and dried oxalate is heated to low redness if it is to be converted into carbonate; but if the oxide is required it is ignited over the blowpipe in a platinum crucible. If boric or phosphoric acids are present this method cannot be employed and the calcium is then precipitated as sulphate by adding dilute sulphuric acid and alcohol.

In presence of much magnesium Sonstadt (C. N. 29, 209) recommends use of potassium iodate, which completely precipitates calcium but not a trace of magnesium.

**Atomic weight of calcium.**—The first accurate determinations were made by Erdmann and Marehand by the ignition of Iceland spar and of pure precipitated calcium carbonate. The results showed that if oxygen = 15.96 the atomic weight of calcium is 39.9. If oxygen = 16 then calcium = 40.0. Subsequent determinations by Baup and Dumas have confirmed these numbers. A. E. T.

**CALICHE.** The term by which the impure native sodium nitrate or Chili saltpetre is known throughout South America (v. SODIUM).

**CALOMEL.** *Mercurous chloride*, v. MERCURY.  
**CALOPHYLLUM INOPHYLLUM.** A tree (Order *Guttifera*) (dilo of Fiji, tamarind of B. Polynesia, and cashumpa of India), the seeds of which yield 60 p.o. of a fragrant green oil, fluid at ordinary temperatures, solidifying when cooled below 10°C. The tree bears fragrant white flowers. The oil, the woodoil or bitter oil of Indian commerce, used for medicine and for lamp oil, is of a greenish tint, and a very little imparts its colour to a whole cask of coconut oil (Ph. [3] 8, 363).

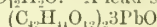
**CALOTYPE** v. PHOTOGRAPHY.

**CALUMBA.** *Colombo, Columbo, Radix Calumbæ, Racine de Colombo* (Fr.); *Kalumba* or *Columbazarra* (Ger.).

The root of the *Jateorhiza palmata* (Miers), an herbaceous climbing plant inhabiting the forests of Eastern Africa (Fl. a. H. 23; Benth. a. T. 13). The fleshy root is sliced transversely and dried. It was introduced into Europe in the seventeenth century as an antidote for poison, and found a place in the London Pharmacopœia of 1788. It possesses mild bitter tonic properties, for which purpose it is now chiefly employed in medicine.

Proximate analyses of calumba were made by Planche (Bl. Ph. 3, 189) and Buchner (Ph. C. 1831, 429). It consists of *bitter matter*, 10-13 p.e.; *yellow resinous extractive*, 5 p.e.; *volatile oil*, traces; *starch*, 30-35 p.e.; *gum*, 4-9 p.e.; and *woody fibre*, 12-39 p.e. The *ash* is about 6 p.e. Tannic acid is absent. The physiologically active constituents of calumba are columbin, columbic acid, and berberine. The first of these, *columbin*,  $C_{21}H_{32}O_{12}$ , was discovered in 1830 by Wittstock (P. 19, 298). It is obtained

from an alcoholic extract, by treatment with ether, in colourless prisms. A somewhat modified method has recently been suggested by Duquesnel (Year Book Pharm. 1887, 148), by which a yield of 0.34-0.4 p.e. is obtained. Columbin is a bitter neutral substance which melts at a gentle heat, and is sparingly soluble in cold water, alcohol, and ether. It may be recrystallised from glacial acetic acid. M.p. 182° (Paternò a. Ogliarolo, B. 12, 685). The crystals were measured by Rose (P. 19, 441). Bodeker (A. 69, 39) made an analysis of columbin and detected *berberine* and another yellow-colouring agent, *columbic acid*, in the root. The acid is obtained as a soluble calcium salt by treating the alcoholic extract with lime water. The addition of hydrochloric acid precipitates it in pale yellow amorphous flakes. Analysed it gave the formula  $C_{12}H_{11}O_{12} \cdot H_2O$ . A lead salt



was prepared.

A. S.

**CAM WOOD** v. SANDERSWOOD.

**CAMPEACHY WOOD** v. LOGWOOD.

**CAMPINE** v. OILS, ESSENTIAL.

**CAMPOL** v. CAMPHORS.

**CAMPHORS.** Camphors are volatile oxygenated hydrocarbons, possessing a peculiar characteristic odour. They are mostly crystalline solids insoluble in water but soluble in alcohol. Except in the case of a few, which are produced artificially, they are obtained from plants where they occur associated with hydrocarbons, from which they are probably derived. Most plants when distilled with steam yield volatile oils composed of heavier oxidised compounds held in solution more or less by lighter hydrocarbons. The former often separate in crystals during the condensation of the oil or afterwards on standing, or they may be obtained by fractional distillation. Most of these oxygenated products, which are very numerous in the vegetable kingdom, and which include nearly all the 'scarcotenes' or solid portions of volatile oils, are camphors in a wide sense of that term. In a narrower meaning the word denotes the well-known laurel camphor of Japan and Formosa, the older camphor of Borneo and Sumatra, and a few other varieties. The earlier Chinese and Arabian notices of camphor refer to the Borneo variety, laurel camphor being a product of a later though unascertained period. Garcia d'Orta mentions the latter as well known in Europe in 1563, and points out, what indeed is true at the present day, that the much more costly Borneo or Sumatra camphor is entirely consumed in the East (cf. Fl. a. H. 510).

The more important camphors, using the term in its larger signification, may be considered in four groups as isomers or homologues of: (1) Peppermint camphor, menthol,  $C_{10}H_{18}O$ ; (2) Borneo camphor, borneol,  $C_{15}H_{26}O$ ; (3) Laurel camphor,  $C_{15}H_{26}O$ ; and (4) Thyme camphor, thymol,  $C_{10}H_{14}O$ . Menthol, the only important member of the first group, is a derivative of the hydrocarbon menthene  $C_{10}H_{18}$ , the members of the borneol group are derivatives of terpenes  $C_{15}H_{26}$ , while the isomers of laurel camphor and thymol are substituted cymenes  $C_{10}H_{14}$ . These hydrocarbons are derivatives of benzene, and the whole class of camphors have therefore the same fundamental structure. For the most part cam-



phors behave like alcohols or phenols, but laurel camphor and the compound menthone appear to be ketones. Just as ketones when reduced by nascent hydrogen yield secondary alcohols, so laurel camphor is converted into borneol, and menthone into menthol. For further discussion of the constitution of camphors *v. Bn.* (3, 262) and Brühl (B. 21, 145 a. 457).

**Peppermint camphor.** *Peppermint camphor*, *Menthol*,  $C_{10}H_{18}O$ . The volatile oils of *Mentha piperita* (Sm.) and *M. arvensis* (De C.), varieties *piperascens* and *glabrata*, consist of the stearoptene, menthol, together with an eleoptene, which, in the case of the English oil, is a mixture of isomeric and polymeric terpenes (Flückiger a. Power, Ph. [3] 11, 220), and in that of the Japanese is chiefly menthone  $C_{10}H_{18}O$  (Beckmann, Jahresb. Pharmak. 1887, 363). The proportion of the menthone in the Chinese and Japanese oils is so great that they are solid at ordinary temperatures, while from the English and American oils only comparatively small quantities can be obtained (*cf.* Todd, Ph. [3] 16, 842). The camphor is extracted either by application of cold and removal of the liquid which adheres to the precipitated mass of crystals by expression, or the oil is submitted to fractional distillation. Compare Dumas (A. 6, 252), Blanchet a. Sell (A. 6, 291), Walter (A. 28, 312; 32, 288), Kane (P. M. 16, 418; A. 32, 285), Oppenheim (A. 120, 351), Beckett a. Wright (C. S. 19, 1), Atkinson a. Yoshida (C. J. 41, 50), and Moriya (C. S. 39, 77). According to Trimble the menthol of the English and American oils *pimenthol* is not identical but differs physically from that of the oils of China and Japan (Am. J. Ph. 1884, 405).

Menthol crystallises in prisms resembling magnesium sulphate. It has the odour and taste of peppermint. M. p.  $36^{\circ}$  (Opp.);  $42^{\circ}$  (B. a. W., A. a. Y.). B. p.  $210^{\circ}$  (Opp., B. a. W., A. a. Y.). Sp.-gr.  $15^{\circ}$ , 0.850 (M.). Lavarotatory (Opp., Arth., A. Ch. [6] 7, 438; Kanonnikoff, J. pr. [2] 31, 348). Heat of combustion (Luginin, A. Ch. [5] 23, 387). Menthol is very slightly soluble in water, but soluble in alcohol, ether, carbon disulphide, petroleum ether, glacial acetic acid, and concentrated hydrochloric acid. It rotates on the surface of water in a similar manner to laurel camphor. Mixed with chloral, thymol, or laurel camphor, menthol reacts, forming a liquid (Kyle, Am. J. Ph. 1885, 429; Becker, Am. J. Ph. 1886, 283). When menthol is boiled with a mixture of sulphuric acid diluted with half its volume of water, it changes to a deep-blue colour (Brit. Pharm. 1885).

Treated with phosphorus pentoxide menthol loses a molecule of water and forms the liquid hydrocarbon *menthene*  $C_{10}H_{18}$  (W.). Concentrated hydrochloric acid (Opp.) or phosphorus pentachloride converts it into *menthyl chloride*  $C_{10}H_{17}Cl$  (W.); *menthyl carbonate*  $(C_{10}H_{17}O)_2CO$  (Arth., A. Ch. [6] 7, 469); *menthyl silicate*  $(C_{10}H_{17}O)_2Si$  (Hertkorn, B. 18, 1695). A nitro-derivative is formed by the action of concentrated nitric acid, which, reduced with nascent hydrogen, yields *menthyl amide*  $C_{10}H_{17}NH_2$  (M.). Menthol reacts with acetic acid producing *menthyl acetate*  $C_{10}H_{17}OAc$  (Opp.; Menschutkin, J. R. 13, 567), and with benzoic acid forming *menthyl benzoate*  $C_{10}H_{17}OBz$  (Arth., A. Ch. [6]

7, 479). Two atoms of hydrogen are removed by treatment with chromic acid, and the liquid *menthone*  $C_{10}H_{16}O$  is formed. According to Beckmann (Jahresb. Pharmak. 1887, 363), menthone is the chief liquid constituent of Japanese oil of peppermint. This compound is related to menthol in the same manner that laurel camphor is to borneol, and can be converted into menthol by the action of sodium and carbon dioxide, just as laurel camphor is converted into borneol (A. a. Y.). When menthol is treated with a large excess of concentrated nitric acid, the oxidation goes further with the formation of a *dibasic acid*  $C_8H_8O_4$  (M.). Hydroxylamine is without action on menthol (Nägeli, B. 16, 498).

Menthol is gradually coming more into use in medicine. It sometimes takes the place of cocaine in the production of local anaesthesia, and it is employed in certain skin diseases.

**Borneo and allied camphors.** *Borneo, Malayan, Barus or Dryobalanops Camphor; Borneol, Camphol*,  $C_{16}H_{14}O$ . This is the product of the *Dryobalanops aromatica* (Gärtn.), a majestic tree indigenous to Sumatra, Borneo, and Labuan, where it often rises without a branch to a height of 150 feet, when its summit is crowned by a magnificent display of foliage 50 to 70 feet in diameter, supporting beautiful white odoriferous flowers (Fl. a. H., 516). The camphor is deposited in crystals in fissures in the old wood, and to obtain it the trees have to be sacrificed. The tree is cut down and the longitudinal fissures opened and the camphor removed. The yield is not more than from 3 to 11 lbs. from large trees. Owing to the reckless manner in which the trees have been destroyed without the planting of others, the forests of Sumatra now contain few that are worth working (Ph. [3] 12, 83). The camphor is best purified by sublimation (Fl. a. H.; Pelouze, A. 40, 326).

Borneol is also a constituent of the following volatile oils: Rosemary, *Rosmarinus officinalis* (L.); Brylants, J. 1879, 944; Fl. a. H., 489; Serpentry root, *Aristolochia serpentaria* (L.), (Spica, G. 17, 314), and Valerian, *Valeriana officinalis* (L.), (Gerhardt, A. 45, 34; Brylants, B. 14, 455; Fl. a. H., 379; Haller, C. R. 103, 151). Besides these natural sources borneol may be obtained by the action of reducing agents on laurel camphor (Berthelot, A. Ch. [3] 56, 78), and in small proportions it is found among the products of the distillation of amber with potash (Berthelot a. Buignet, A. 115, 245).

Borneol is harder and less volatile than laurel camphor and does not sublime in the bottles in which it is kept. It has a peppery camphoraceous odour and burning taste. M. p.  $206-207^{\circ}$  (Plozman, Ph. [3] 4, 709). B. p.  $212^{\circ}$  (Pelouze). Sp.-gr. 1.011 (Pl.). Dextrorotatory (Kachler, A. 197, 99; Mongolfier, B. 10, 729). Refraction coefficient (Kanonnikoff, J. pr. [2] 31, 348). It is very slightly soluble in water, but dissolves readily in alcohol and ether. Removal of a molecule of water by phosphoric anhydride leaves the solid terpene *borneo-camphene*,  $C_{16}H_{16}$  (Wallach, A. 230, 239). Concentrated hydrochloric acid (Berthelot, A. 112, 366) or phosphorus pentachloride (Kachler) reacts with formation of *bornyl chloride*  $C_{16}H_{17}Cl$ . *Bornyl acetate*  $C_{16}H_{17}OAc$  is a constituent of valerian oil (Brylants), and may be produced by the

action of acetic anhydride on borneol (Montgolfier, A. Ch. [5] 14, 50) and in a similar manner *bornyl benzoate*,  $C_{16}H_{17}.OBz$  is obtained (Berthelot). Sodium reacts on borneol in solution in benzene with the formation of a crystalline *sodium salt*,  $C_{10}H_{17}.ONa$  (Kachler a. Spitzer, M. 2, 235). The *methyl ether*  $C_{10}H_{17}.OMe$  is formed by acting on the sodium salt with methyl iodide (Baubigny, Z. 1868, 299). Nitric acid oxidises borneol with formation of *dextrorotatory camphor*,  $C_{10}H_{16}O$ , in the first instance, and the reaction proceeding further *camphoric acid*,  $C_{10}H_{16}O_4$ , and other products result (Laurent, A. 22, 135; Pelouze, A. 40, 328; Kachler, A. 193, 143).

*Camphors isomeric or homologous with borneol.* Artificial *Lavoborneol*  $C_{10}H_{18}O$  is produced together with dextroborneol in the reduction of laurel camphor (Montgolfier, A. Ch. [5] 14, 21).

*Cineol*  $C_{10}H_{18}O$  is the chief constituent of the volatile oils of *santonica*, *Artemisia maritima*, var. *Stectmanniana* (Besser) (Kraut, J. 1862, 460; Krant a. Wahlforss, A. 128, 293; Hell a. Stürcke, B. 17, 1970; Wallach a. Brass, A. 225, 291), and of *cajeput*, *Melaleuca cajuputi* (Roxb.), *cajeputul* (Wallach, A. 225, 315). *Cineol* is also contained in the volatile oils of *Eucalyptus globulus* (Labill.) (Faust a. Homeyer, B. 7, 1429; Jahns, B. 17, 2943) and of *rosemary*, *Rosmarinus officinalis* (L.) (Weber, A. 238, 95). Artificially it may be obtained by the action of aqueous phosphoric acid on terpinolol, or in small proportions by treating terpinhydrate with mineral acids (Wallach, A. 239, 18). B.p.  $176^\circ$  (Wallach),  $172.5^\circ$  (H. a. S.). It does not alter a ray of polarised light. The terpenes *cineol*,  $C_{10}H_{18}O$ , and *dicineol*,  $C_{20}H_{32}O_2$ , result from the action of phosphoric anhydride (H. a. S.). Oxidised by permanganate, *cineolic acid*  $C_{10}H_{16}O_3$ , and other products are formed (Wallach a. Gilde-meister, A. 246, 268). *Cineol* absorbs hydrochloric acid gas, forming the crystalline *hydrochloride*  $C_{10}H_{17}O.HCl$  (Hell a. Ritter, B. 17, 1977). A characteristic reaction for cineol is that, shaken with a saturated solution of iodine in potassium iodide, there is formed a glutinous mass of minute shining greenish crystals (Bn. 3, 267).

*Colophene camphor*  $C_{10}H_{18}O$  resembles borneol and is deposited in crystals from a fraction of that portion of the crude product of the action of sulphuric acid on turpentine which is volatile in a current of steam (Armstrong a. Tilden, C. J. 35, 752). *Maddercamphor*  $C_{10}H_{18}O$  is contained in the fusel oil of the crude spirit obtained by the fermentation of the sugar of madder (Jeanjean, A. 101, 95). *Ngai camphor*  $C_{10}H_{18}O$  is a product of the *Blumea balsamifera* (De C.). It is nearly related to, if not identical with, madder camphor, and in most respects behaves like borneol. It is levorotatory, and when oxidised it yields a levorotatory isomeride of laurel camphor. M.p.  $204^\circ$  (Hanbury a. Plowman, Ph. [3] 1, 709; Flickiger, Ph. [3] 4, 828). *Terpene hydrate*  $C_{10}H_{18}O$ , the *Terpinolol*, *Terpinolol*, and  $\alpha$ - and  $\beta$ -*Borneols* are also isomerides of Borneo camphor (Bn. 3, 267).

The following volatile oils contain liquid isomerides of borneol:—*Buchu leaves*, *Barosma betulina* (Bart. a. Wendl.), *B. crenulata* (Hooker),

*B. serratifolia* (Willd.), contain an oil  $C_{10}H_{18}O$  boiling at  $205\text{--}210^\circ$  together with *diosphenol*  $C_{11}H_{18}O_2$  (?), a crystalline camphor melting at  $83^\circ$  and boiling at  $233^\circ$  (Flickiger, J. 1880, 1081). Diosphenol is probably identical with the compound  $C_{10}H_{18}O_2$ , obtained by Spica from *B. crenata* (L.) which melted at  $82^\circ$ , boiled at  $220^\circ$  (G. 15, 195); Citronella, *Andropogon Nardus* (L.) (Wright, Ph. [3] 5, 233); Coriander, *Coriandrum sativum* (L.) (Kawahier, J. 1852, 624; Grosser, B. 14, 2485); *Galangal*, *Alpinia officinarum* (Hance) (Vogel, B. J. 24, 479); Geranium, *Andropogon Iwarancusa* (L.), *A. Schenanthus* (L.) (Jacobson, A. 157, 232); *Pelargonium Radula* (Aiton) (Gintl. J. 1879, 941); Hops, *Humulus Lupulus* (L.) (Wagner, J. 1853, 516; Personne, J. 1854, 654; Ossipoff, J. pr. [2] 28, 448); Lemon, *Citrus Limonum* (Risso) (Tilden, Ph. [3] 9, 654); Sage, *Salvia officinalis* (L.), *Salviol* (Muir, C. J. 37, 678); Tansy, *Tanacetum vulgare* (L.) (Bruylants, B. 11, 452). *Angustura*, *Galipea cusparia* (St.-Hil.), yields a volatile oil containing  $C_{13}H_{22}O$  which is a higher homologue of Borneo camphor (Herzog, J. 1858, 444).

**Common and allied camphors.** *Common Camphor*; *Laurel Camphor*; *Camphre*, Fr.; *Campher*, Ger.  $C_{10}H_{16}O$ . Common camphor is contained in all parts of the camphor laurel, *Cinnamomum camphora* (Nees a. Eberm.), a tree inhabiting Japan, Formosa, and central China, and cultivated for its foliage in the South of Europe and generally in warm climates. It occurs also as a constituent of the volatile oils of Lavender, *Lavandula vera* (De C.) (Dumas, A. 6, 248; cf. Fl. a. H. 478); Rosemary, *Rosmarinus officinalis* (L.) (Lallemand, A. 114, 197); Sage, *Salvia officinalis* (L.) (Muir, C. J. 37, 678); and Spike, *Lavandula spica* (De C.) (Lallemand). Artificially common camphor may be produced by the oxidation of borneol (Pelouze, A. 40, 328) and many of its isomerides (Rochleder, A. 44, 1; Faltin, A. 87, 376). The camphor of commerce is, however, obtained entirely from the camphor laurel. It is prepared in Japan and Formosa in a crude state, and is refined in Europe and America.

In Formosa the camphor manufacture has fallen off to such an extent that the Chinese government has recently taken over its management in the hope of reviving it as a state monopoly (S. C. 1. 1887, 391). The trees grow on both sides of the central chain of mountains, where they are found as high up as elevations of 2,000 feet. The wood is collected along the boundary separating the Chinese coast settlements from the native domain in the interior, and it is either distilled with steam in a very crude manner on the spot or is taken into the towns where a less wasteful process of distillation is carried out. The trees are not necessarily cut down, but the wood chopped out in the form of chips by means of a long-handled gongce. A wooden boiler in the form of a trough is made in the woods, often out of a hollow trunk of a tree. This is coated with clay and covered with a flat piece of wood containing a row of ten openings for jets of steam to escape. Water is poured in and a fire lighted beneath. Chips of camphor wood are then placed above each of the ten openings in such a manner that the steam passes

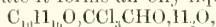
amongst them. Over each pile is inverted an earthen pot in which the camphor volatilised and carried upwards with the steam condenses in minute crystals, and out of which it is scraped every few days. Sheds are usually built over four such stills and the whole is moved from one place to another as the camphor wood is exhausted (Fl. a. II., 513). A drawing of a somewhat superior form of still, doubtless one of those in use in the towns, is given by Flückiger (Ar. Ph. 1879, 214). The camphor thus obtained is brought down to the coast in baskets holding half a pecul (pecul is  $133\frac{1}{2}$  lbs.), where it is placed in vats to drain, or the oil which it still retains to the extent of 20 p.c. is removed by hydraulic pressure. It is exported in boxes lined with lead or tin-plate and holding about a pecul each. In the market it is known as Formosa or Chinese camphor. It is usually wet, and consists of small grains of a light-brown colour. The Chinese do not value it, and for their own purposes they import the more costly camphor of Borneo (cf. Ph. [3] 13, 223).

The procedure is somewhat different in Japan. The trees, which should not be less than a hundred years old, are cut down and chopped into small pieces. Metal boilers have long been in use (Künfer, 1712; Fl. a. H.), still at the present day very crude wooden receivers may sometimes be seen. Compare drawing by Flückiger (Ar. Ph. 1879, 214). A still is described by the United States Consul Jones of Nagasaki (Y. B. Ph. 1884, 212), which consists of a metal boiler over which is fixed a tub containing the camphor chips, and so arranged that the steam passing through it carries the camphor and oil vapours into a first and second wooden condenser. In the second the camphor crystallises amongst straw in an upper compartment, and the water and oil collect below. An improved form of apparatus is described with a drawing by Oishi (S. C. I. 1884, 353). An iron boiler is placed over a furnace, and to this is fitted a wooden tub containing the camphor chips and constructed so that the steam after traversing the chips escapes together with the oil and camphor by a bamboo or wooden pipe to a special form of condenser. The boiler is circular with a diameter of 3 feet. The tub or steam jacket has a diameter of 2 feet 10 inches below and 1 foot 6 inches above, and is 4 feet high. The condenser is a flat rectangular wooden vessel fitted inside with a number of partitions so as to expose as large a surface as possible for condensation. It is cooled by being placed horizontally in a shallow trough of cold water in which it is partly submerged. Another somewhat smaller trough is laid on the top of it, and cold water is arranged to flow through both during the operation. The charge of 120 kilos of chips is exhausted in 24 hours and has to be renewed, but the contents of the condenser need only be removed every 5 or 10 days. This is filtered to separate the solid camphor from the oil which still holds some 20 p.c. of camphor in solution. This is obtained by fractional distillation and the application of cold to the distillate. The yield of camphor is greater in winter than in summer, while the reverse is true of the oil. In summer a charge of 120 kilos of wood gives 2·4 kilos or 2 p.c. of camphor, and

1·8 litres of oil, in winter 3 kilos or 2·4 p.c. of camphor and ·5 to ·7 litres of oil. The oil after separation of the dissolved camphor is applied to illuminating and other purposes. The camphor is exported in double tubs, one inside the other, and containing a pecul each. It is drier and lighter in colour than Formosa camphor, and often has a pinkish hue. It fetches a somewhat higher price in the market.

Crude Japan or Formosa camphor contains from 2 to 10 p.c. of impurities insoluble in alcohol. It is refined in this country, on the Continent, and in the United States, and also to some extent in India. In Europe the crude product is mixed with a little charcoal, sand, iron filings, or quick lime, and sublimed. The operation is generally performed in glass flasks 'bomboloes,' in the upper half of which the camphor condenses in the form of large coneavo-convex cakes with a hole in the middle which corresponds to the opening in the neck of the flask. To remove the cakes, which generally weigh from 9 to 12 lbs., the flasks are broken. The sublimation requires great care owing to the inflammability of camphor vapour, and the right temperature to be employed is a matter of importance. The flasks containing the crude camphor are rapidly heated on a sand bath to 120–190° to remove water, then the temperature is allowed to rise slowly to about 204°, and maintained at that for 24 hours. (Cf. Fl. a. H., 514.)

Purified camphor consists of colourless translucent masses traversed by numerous cracks, or, when slowly condensed, of hexagonal crystals. It can be broken, but is too tough to admit of being powdered by trituration. This may, however, be readily effected if a little alcohol be added, which escapes again during the operation. Camphor is used in medicine for its stimulant and antiseptic properties, and it is largely consumed by the natives of India. Sp.gr. 0·992 (10°); m.p. 175°; b.p. 204°. It sublimes to some extent at ordinary temperatures (cf. Folger, Y. B. Ph. 1886, 232). Dextro-rotatory (Landolt, A. 189, 334). Refraction coefficient (Kanonnikoff, J. pr. [2] 31, 348). Camphor, in common with chloral hydrate and some other substances, rotates in a peculiar manner on the surface of water (Tomlinson, P. M. [1] 46, 376; Ph. 4, 654 a. 672; C. N. 36, 215; 37, 72; 52, 50). Water dissolves it very sparingly, but it is readily soluble in alcohol, ether, and chloroform. Mixed with chloral hydrate it forms an oily liquid,



which has been employed in medicine (Brown, Ph. [3] 4, 729; Saunders, Ph. [3] 7, 89; Caze-neuve a. Imbert, Bl. [2] 34, 209; Zeidler, J. 1878, 645; Albright, Am. J. Ph. 1886, 282). Similar combinations take place between camphor and chloral alcoholate (Zeidler), phenol (Flückiger, Ph. Chem. 2, 450), menthol (Kyle, Am. J. Ph. 1885, 429), and thymol (Symes, Ph. [3] 9, 598).

Phosphoric anhydride removes water from camphor, forming *cymene*  $\text{C}_{10}\text{H}_{16}$ , together with other hydrocarbons (Armstrong a. Miller, B. 16, 2259). With phosphorus pentachloride it yields *camphor dichloride*  $\text{C}_{10}\text{H}_{14}\text{Cl}_2$ . *Nitro-camphor*,  $\text{C}_{10}\text{H}_{13}(\text{NO}_2)\text{O}$ , is prepared by reduction



of chloronitro-camphor (Cazeneuve, Bl. 47, 920; 49, 92; Schiff, B. 13, 1403), and this by treatment with sodium amalgam is converted into *amido-camphor*  $C_{10}H_{12}(NH_2)O$  (Schiff). *Mono-, di-, and trichloro-camphor* (Bn. 3, 271). Of the bromine derivatives, *monobromo-camphor*  $C_{10}H_{17}BrO$  is employed in medicine, and is an article of trade. It is prepared by treating camphor with bromine at  $130^\circ$ , and crystallising the mass obtained from petroleum ether. It may be purified by recrystallisation (Maisch, Am. J. Ph. 44, 177; Gault, l'Union Ph. 15, 266; Keller, J. 1880, 726). From alcohol it crystallises in colourless prisms or needles, from petroleum either in long flat prisms or glossy scales. Monobromo camphor has a weak camphoraceous odour and taste. M.p.  $76^\circ$ ; b.p.  $274^\circ$  (Perkin, A. Spl. 4, 125). It is insoluble in water, but soluble in alcohol, ether, chloroform, benzene, the fixed oils, and sulphuric acid. By the action of reducing agents, camphor is converted into *borneol*. This may be accomplished conveniently by adding sodium to an alcoholic solution of camphor (Jackson a. Menke, Am. 5, 271; Jackson, Am. 6, 406). Hot alkaline permanganate (Grosser, B. 14, 2507), or nitric acid (Kachler, A. 162, 262; 193, 143), oxidises camphor with the formation of *camphoric acid*,  $C_9H_{14}(COOH)_2$ .

*Camphors isomeric or homologous with common camphor*. Isomerides of common camphor are: *Anise-camphor* formed by the action of nitric acid on anethol, b.p.  $190-193^\circ$  (Landolph, B. 13, 145); *Inactive camphor*, obtained by oxidising inactive camphene with chromic acid (Armstrong a. Tilden, B. 12, 1756); *Levo-camphor* produced, according to Riban (Bl. 24, 19), by the oxidation of levo-camphene (but v. A. a. T.) and occurring in volatile oil of Feverfew, *Pyrethrum Parthenium* (Sm.) (Chautard, C. R. 37, 166), differs only from common camphor in its behaviour towards polarised light; and *Carveol* (Leuckart, B. 20, 114).

The following are the most important volatile oils which contain isomerides of camphor: *Arbor vite*, *Thuja occidentalis* (L.), *Thujol* (Jahns, Ar. Ph. 221, 748); Chamomile, *Anthemis nobilis* (L.), *Anthemol* (Köbig, A. 195, 95); Cowbane, *Cicuta virosa* (L.) (Trapp, J. 1858, 444); Galbanum, one of the products of the distillation of galbanum (Kachler, B. 4, 39; Mössmer, A. 119, 257); German Chamomile, *Matricaria Chamomilla* (L.) (Kachler, B. 4, 36; Bizio, J. 1861, 681); Hyssop, *Hyssopus officinalis* (L.) (Schmidt, Lehrb. Ph. Ch. 2, 830); Elecampane, *Inula Helenium* (L.), *Inula*, or *Alant Camphor*, a liquid with the odour of peppermint, which when treated with phosphoric anhydride yields eymene, and with chromic acid, terephthalic acid (Kallen, B. 9, 154); Nutmeg, *Myristica fragrans* (Houtt.), *Myristicol* (Wright, B. 6, 147); Pennyroyal, *Mentha pulegium* (L.) (Kane, A. 32, 286), and the nearly related *Pulegium Micranthum* (Claus) (Butleroff, J. 1854, 594); Pichurin Beans, *Nectandra Puchury* (Nees), (Müller, J. 1853, 514); Sage, *Salvia officinalis* (L.), m.p.  $174^\circ$ ; b.p.  $205^\circ$  (Muir, C. J. 37, 678); and Wormwood, *Artemisia Absinthium* (L.), *Absinthol* (Beilstein a. Kupffer, A. 170, 290).

The more important homologues of common camphor are:

*Matico camphor*  $C_{12}H_{20}O$ , contained in the volatile oil of matico leaves, *Piper angustifolium* (Ruiz a. Pavon), which on standing deposits the camphor in crystals, m.p.  $94^\circ$ . Concentrated hydrochloric acid colours it intense violet, changing to blue and green (Kügler, B. 16, 2841).

*Cedar camphor*  $C_{11}H_{20}O$ , a crystalline mass obtained from the volatile oil of *Juniperus Virginiana* (L.), m.p.  $74^\circ$ , b.p.  $282^\circ$ . Yields *cedrene*  $C_{15}H_{26}$ , when treated with phosphoric anhydride (Walter, A. 39, 247; 48, 35).

*Cubeb camphor*  $C_{11}H_{20}O$ , a constituent of the volatile oil of the old fruits of the *Piper cubeba* (L.). The crystals melt at  $68.7^\circ-70^\circ$  (W.),  $65^\circ$  (S.),  $67^\circ$  (S. a. W.). B.p.  $148^\circ$  (S.). Dehydrated by sulphuric acid, *cubebene*  $C_{11}H_{20}$  is formed (Blanchet a. Sell, A. 6, 294; Winckler, A. 8, 203; Schmidt, Z. 1870, 190; Schaer a. Wyss, J. 1875, 497).

*Ledum camphor*  $C_{15}H_{26}O$  (?) obtained from the volatile oil of Marsh Tea, *Ledum palustre* (L.). Needles, m.p.  $104-105^\circ$ , b.p.  $292^\circ$ . By the action of phosphoric anhydride, the *sesquiterpene*  $C_{15}H_{24}$  is formed (Rizza, J. R. 19, 319; Trapp, B. 8, 542; Hjelt a. Collan, B. 15, 2501).

*Patchouli camphor*  $C_{15}H_{26}O$  (?) a crystalline camphor contained in the volatile oil of *Pogostemon patchouli* (Pelletier); m.p.  $54-59^\circ$ , b.p.  $206^\circ$ . By the action of acetic anhydride it loses water and forms *patchoulene*  $C_{15}H_{24}$  (Gal, C. R. 1869, 68, 406; Montgolfier, Bl. 28, 414; Maisch, Am. J. Ph. 1884, 84).

*Sandalwood camphor*, *Santalol*  $C_{15}H_{26}O$ , a liquid camphor obtained from the volatile oil of *Santalum album* (L.), b.p.  $310^\circ$  (Chapoteaut, Bl. 37, 303).

**Thyme and allied camphors.** *Thyme camphor*, *Thymol*  $C_{10}H_{14}O$ , i.e.  $C_6H_5.Me.(OH).Pr.$  [1:3:4].

Thymol is a constituent of the volatile oils of Ajowan, *Carum ajowan* (Benth. a. Bork.) (Haies, C. S. Mem. 8, 289; Stenhouse, A. 98, 269, a. 307; Müller, B. 2, 130); Garden Thyme, *Thymus vulgaris* (L.) (Dover, A. 64, 374; Lallemand, A. Ch. [3] 49, 148); Horse Mint, *Monarda punctata* (L.) (Arppe, A. 58, 41) and together with carvacrol in Wild Thyme, *Thymus serpyllum* (L.) (Jahns, B. 15, 819; Febre, J. 1881, 1028). To extract it the oils are shaken with a solution of caustic soda, when the thymol passes into the aqueous portion in the form of a soluble sodium salt and is thus separated from the hydrocarbons. The alkaline solution is acidified with hydrochloric acid, which precipitates the crude camphor. It may then be purified by crystallisation from glacial acetic acid or alcohol. Another plan is to submit the oils to fractional distillation and to precipitate the thymol from the heavier portions of the distillate by the application of cold.

Thymol has the odour of thyme and a warm pungent taste; m.p.  $50^\circ$ , b.p.  $222^\circ$  (Stenhouse),  $230^\circ$  (Lallemand). It is sparingly soluble in water, but very soluble in alcohol, ether, and alkaline solutions. It forms a liquid with menthol (Kyle, Am. J. Ph. 1885, 429), camphor (Symes, Ph. [3] 9, 598), berberine (Lloyd, New Remedies, 1881, 195), but not with chloral hydrate (Symes, cf. Mazzara, G. 13, 272). If a solution containing thymol be warmed with half its volume of glacial acetic acid together with

more than its volume of sulphuric acid, a deep red-violet colour is developed. This reaction is obtained even in very dilute solutions (Robbert, J. Th. 1881, 109; Wolff, Fr. 22, 96). For other test reactions see Störmer (Ar. Ph. [3] 25, 36; Ph. Z. 31, 744; Hirschsohn, Ph. [3] 12, 21). For colour reactions with sugars v. Lindo (C. N. 55, 239).

Phosphoric anhydride splits the thymol molecule into *propylene*  $C_3H_6$  and *m-cresol*  $C_6H_4Me.OH$  [1:3]. Phosphorus pentasulphide deoxidises it with the formation of *p-cymene*  $C_6H_4.Pr.Me$  [1:4] (Fittica, A. 172, 305). Well-defined salts are formed with *sodium*  $C_{10}H_{13}.ONa$ , *mercury*  $C_{10}H_{13}.HgOH$ , and *aluminium*  $(C_{10}H_{13}O)_3Al$ .

By the action of nitrous acid on thymol, *isomethoxythymol*  $C_{10}H_{12}(N.OH)O$  is obtained in yellow needles (Schiff, B. 8, 1500) and from this compound *nitrothymol*  $C_{10}H_{13}(NO_2)O$  (Schiff) and *amidothymol*  $C_{10}H_{13}(NH_2)O$  are derived. *Halogen derivatives* (Bu. 3, 498); *Methyl ether*  $C_{10}H_{13}OMe$  (Engelhardt a. Latschinoff, Z. 1869, 43); *Ethyl ether*  $C_{10}H_{13}.OEt$  (Jungfleisch, Z. 1865, 532); *Acetate*,  $C_{10}H_{13}.OAc$  (Paterno, Bl. 25, 32); *Benzoate*,  $C_{10}H_{13}.OBz$  (E. a. Z.); *Carbonate*  $(C_{10}H_{13}O)_2CO$  (Richter, J. pr. [2] 27, 505); *Phosphates*  $(C_{10}H_{13}O)_3PO$  (E. a. Z.).  $(C_{10}H_{13}O)_2HO.PO$  (Kreysler, B. 18, 1705; Discaizo, G. 15, 280), and  $(C_{10}H_{13}O)(HO)_2PO(D$ , Bn. 3, 496).

Thymol is used in medicine as an antiseptic.

*Camphors isomeric with thyme camphor*. *Carvol*  $C_{10}H_{18}.OH$  is a liquid isomeride contained in the following volatile oils: Caraway-seed, *Carum carui* (L.) (Völekel, A. 85, 246); Dill-fruit, *Peucedanum graveolens* (Hiern) (Nietzki, N. Handb. Chem. 2, 986); Spearmint, *Mentha viridis* (L.) (Gladstone, J. 1863, 548), and Crisped Mint, *Mentha crispata* (L.) (Schmidt, Lehrb. Ph. Chem. 2, 815). Carvol is distinguished from other constituents of volatile oils by its power of combining directly with sulphuretted hydrogen to form the crystalline *hydrosulphide*  $(C_{10}H_{11}O)_2H_2S$  (cf. Flückiger, B. 9, 468; Bn. 3, 501). *Carvacrol*, *cymphenol*  $(C_6H_4.Me.(OH).Pr)$  [1:2:4] is a thick oil closely related chemically to thymol. It is formed by distilling carvol in presence of solid phosphoric acid or caustic potash, and occurs in the following volatile oils: *Origanum hirtum* (L.) (Jahns, J. 1879, 942); *Satureja hortensis* (L.) (Jahns, B. 15, 816); *S. montana* (L.) (Haller, Bl. 37, 411); and *Thymus serpyllum* (L.) (Jahns, Bn. 3, 500).

**CAMPOBELLO YELLOW** v. NAPHTHALENE

COLORING MATTERS.

**CANADA BALSAM** v. BALSAMS; and OLEO-RESINS.

**CANADA PITCH** or **HEMLOCK SPRUCE RESIN** v. RESINS.

**CANADOL**. Petroleum ether or ligroin. That portion of refined petroleum which boils at about 60° and has sp.gr. of '65 to '70 consists mainly of normal hexane (v. PARAFFIN; and PETROLEUM).

**CANARIN**. A yellow colouring matter obtained by the action of bromine or a mixture of potassium chlorate and hydrochloric acid upon potassium or ammonium thiocyanate; it probably consists of perthiocyanogen  $C_3HN_2S_3$  (H.

Schmid, D. P. J. 251, 41). (For details of mode of preparation v. D. P. J. 253, 130, also S. C. I. 3, 476.) Cloth dyed with canarin resists light and soap. Neither concentrated acids nor alkalis destroy it or dissolve it out of the fibre. Bleaching powder has no action upon it. Acts as a mordant for basic aniline dyes.

**CANDLES**. Candles are among the most ancient forms of illuminants. The excellence of a candle depends on the nature of the wick and of the combustible matter, and on the manner and extent in which these are apportioned. In the following list, the torch must be regarded as a huge wick with the minimum amount of combustible matter; this proportion being gradually altered until the present ratio of about 1 part wick to 50 parts of combustible matter is reached.

*Table showing the stages in the development of candles.*

**Torch**. Pine branches or slips (Lat. *teda*), saturated, naturally or artificially, with resinous or fatty matter.

**Link**. Rope-strands steeped in resin, tar, or pitch; in olden times, doubtless, with asphalt or bitumen.

**Flambeau**. A core of hemp, soaked in resin and coated with crude bees-wax. Later the outer coat was of bleached wax.

**Dips**. Wicks of rush-pith (rush-lights), crude flax or cotton, and subsequently of twisted cotton yarn, coated with wax or tallow by repeated dippings.

**Moulds**. (Introduced about the 15th century by the Sieur de Brez.) Hard tallow, spermaceti, stearin, or paraffin, cast round the wick in a mould.

In addition to these varieties may be mentioned *rolled*, *poured*, and *drawn* candles.

**Dips**, the cheapest, as well as the oldest form of candle, were made until comparatively lately of tallow or household grease. Wax candles were mostly poured, drawn, or rolled. The great advantage of the 'dip' lies in the ease with which it can be made. The thrifty housekeeper was wont to set aside the superfluous kitchen fat for melting day, when part went to make soap whilst the harder portions were formed into candles. The fat was thrown into boiling water and boiled three or four times with a little salt to 'render' it. The dirt and impurities being removed by subsidence, the clean liquid fat was run through a strainer into the candle pan. Some skill and experience were required to regulate the temperature of the melted fat. If too hot, the liquid fat would run off the wicks; if too cold, the material would congeal too quickly and adhere irregularly and in lumps to the wicks. In households these would be rushes, divested of their peel, with the exception of a thin strip which was left to give strength to the pith. These were usually tied in bunches of four, so that one wick could be held between each pair of fingers, and thus be immersed in the liquid fat. A short time was allowed after each dip to cool the last coat. Four dippings mostly sufficed; when the finished candles were hung up in an airy loft to harden and whiten.

In dips as manufactured on a large scale the wicks are of twisted cotton, and are strung on rods, each rod holding eight. The workman,

holding an end of the rod in either hand, first immerses the wicks in very hot tallow, in order that their fibres may be thoroughly saturated, and then, as each rod is ready, it is slid on to a cross frame to cool; when the wicks are re-dipped in tallow of about 16° C. (60° F.) till the desired weight is obtained.

Many devices exist for reducing labour and ensuring uniformity of result in manufacturing dippers. Of these contrivances the 'Edinburgh wheel' is the best known. It consists of a long pole, pivoted vertically, and having mortises cut about its centre through which pass long wooden bars, each pivoted at its centre on an iron pin. These bars carry frames at their extremities, each of which, in their turn, holds, say, eight wicked rods. The post revolves, and as each bar with its frame passes over the melting pan, it is pulled down, so as to immerse the wicks. The opposite frame restores equilibrium, and the rotation and dipping are proceeded with until the proper weight is obtained, which is signalled by some contrivance on the post, itself the object of much invention. The most perfect apparatus of this kind was patented a few years ago, and worked by Price's Candle Company at the Inventions Exhibition in London in 1885.

**Rolled, poured, and drawn candles.** Rolled candles are now almost obsolete. Formerly, the larger sizes of church candles were made by

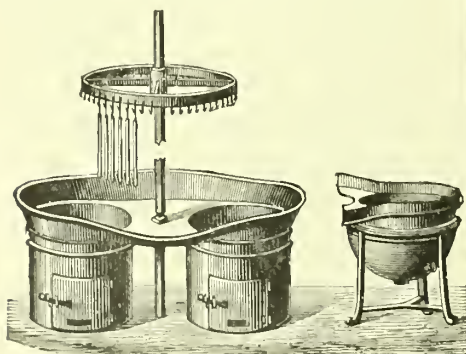


FIG. 1.

'rolling' a cake of warm wax, kneaded until it was plastic, round a wick, and imparting the necessary smoothness and uniformity by means of a rolling-pin. This process has now been entirely superseded by that of pouring. 'Drawing' is resorted to only in the case of small sizes and tapers. In pouring, a similar apparatus to that used in dipping is employed, but instead of the wicks being dipped, the melted wax is poured over them whilst the frame is kept in rotation (fig. 1). In the larger sizes the wicks have to be reversed from time to time to ensure a uniform thickness. The workman ascertains the correct dimensions by measuring with a piece of tape. After every two or three pourings, according to the weather, the hoops are hung in a current of air to cool. When the candles are of the requisite thickness, they are severed from the frame and placed on a smooth marble slab. The operator then rolls them to and fro under a board, on which he leans

with his full weight. By this process, which requires much skill and practice, the irregularities are smoothed away, and the candles, in the hands of a skilful workman, assume the evenness of outline of moulded candles, with a peculiar softness, indescribable, though unmistakable when once identified. The ends of the candles are now cut clean with a sharp knife, and their tips shaped with the finger and a small strip of wood.

It will be readily seen that this process, which involves much skilled labour, must render wax candles very expensive. They are, indeed, the most costly form of illuminant; so that but few private persons can or will afford to burn them. Their use is confined to churches and, to a less extent, to carriage lamps, in which formerly no other candle could be employed, by reason of the strong spring, although now several efficient substitutes exist and are coming into favour.

To understand the favour which wax continued to enjoy long after the introduction of stearin and paraffin, which are not only much cheaper, but give a better light, we must take several circumstances into account. The first and, doubtless, the most cogent fact lies in the sharp contrast which formerly obtained between wax and tallow, a contrast which finds mention in many a tale of social life, even as far back as the times of Haroun Alraschid. The candle at one period was absolutely the only means of illumination available, and formed a very considerable item in the household expenses. As only the rich could afford this luxury, the wax candle became intimately associated with the other signs of wealth, as essential, indeed, as arms or silver plate. The introduction of spermaceti in the middle of the last century greatly influenced the use of wax, and this was quickly followed by the adoption of gas in houses. Within the last few years the electric light has replaced both wax and spermaceti in houses where for centuries no other light was known; and before long a wax candle in a private house will be as rare as a tinder box.

To adapt the bees-wax as it comes from the hive to the requirements of the chandler but little is needed beyond the ordinary cleansing processes. The clean wax is run from the copper over a rapidly rotating drum into cold water, by which means it becomes divided into fine shavings. These are exposed to the influences of sun and air for several weeks, with occasional re-meltings and pourings, after which the now cream-white wax is ready for use.

**Drawn candles** are made by drawing a considerable length of wick through a pan of wax (fig. 2), maintained at a regulated temperature by fire or steam. The wick is wound from one drum on to another. As it leaves the pan it traverses a plate perforated with holes increasing from half an eighth to half an inch in diameter, whereby the superfluous wax is stripped off, the coated wick as it emerges being of the diameter of the hole. When the wick is all wound off, the drums are reversed, the end of the coated cotton passed through the hole next in size, and the operation continued till the requisite size is obtained. This is seldom over half an inch, as the risk of cracking increases considerably with the diameter of the cable. In fact, this process is resorted to



mainly for manufacturing 'spills' or lighting-wicks and the little tapers used for decorating Christmas-trees, but here also stearin in the first and paraffin in the last have gradually displaced wax.

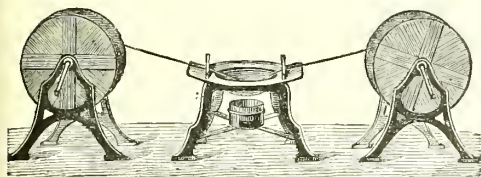


FIG. 2.

*Mould candles.*—Before describing the manufacture of mould candles—the chief variety of candle now made—it is necessary to devote some space to the wick, which is to the candle what the burner is to the gas. Till about 1820, the only wicks used were made of twisted cotton yarn, still to be seen in tallow dips. No means for consuming the wick being employed, snuffers had to be used to remove the charred and glowing end. Several expedients were devised to bring the wick automatically into contact with the air, and thus cause it to be consumed as the candle burnt. The best of these consisted in twisting the wick round a rod, and while in a state of tension, coating one side with size or other stiffening. This imparted a tendency to turn outwards and curl over, which to a great extent obviated the use of snuffers. Mr. Palmer invented a simple means for achieving the same result more thoroughly. He introduced a fine thread coated with metallic bismuth into the substance of the wick, which thread he called the 'doctor.' When ignited, the easily fusible metal formed a globule on the end of the cotton, which by its weight bent the wick out of the flame into the air, when the oxygen could combine with the incandescent carbon, whilst the bismuth was volatilised. So successful was this device, that Palmer's 'Metallic Wick' candles achieved great popularity, especially for burning in candle-lamps, for which large candles sometimes weighing two pounds were employed.

But the introduction of 'braided' or 'plaited' wicks by Cambeccres rendered such precautions unnecessary, the flat form of the wick, as now made, imparting a sufficient tendency to curve. Now all except tallow candles are provided with these cores.

Before the wick can be used by the candle-maker, it has to be 'pickled,' i.e. soaked in a solution of certain chemicals, which vary with the nature and purpose of the cotton. In fact, the preparation of these solutions forms one of the chief items in a good candle-maker's education, and to carry it out thoroughly demands no little chemical knowledge. For the wick itself varies much in its composition, especially as regards the percentage of mineral matter. The plait, too, will vary in tightness, however carefully woven. Then again, a paraffin candle requires a tight plait, to check a too rapid supply of the liquid fuel. A wax or sperm candle, on the other hand, where the melted material is less mobile, or has a less tendency to smoke, needs a loose texture. The nature of the combustible, its melting-point, viscosity, and burning powers;

the composition of a suitable material from several sources, the selection of a wick that in number of threads, structure, and substance is adapted to the special material chosen, the subsequent treatment of this with such salts as will correct or enhance its tendencies; these are some of the points which must be considered before proceeding with the more mechanical operations.

The wicks, which arrive at the factory from the cotton-spinner's in hanks, are placed two or three days before being wanted in the appropriate solution. Of these solutions, the object is to counteract either 'ashing' or 'smoking,' two great evils to which the candle is liable. Borax, nitre, sal ammoniac, potassium chlorid or chlorate, and, more rarely, phosphorus compounds, are the principal salts employed for this purpose; though almost every manufacturer has his own receipt. The proportion of the salt to water is usually about 2 oz. to 1 quart. The wicks are steeped in the solution for about twenty-four hours, after which they are placed on a perforated shelf to drain off the bulk of the liquid and then transferred to a centrifugal machine rotating at a speed of nearly 1,000 revolutions a minute, where the residual water is expelled without the slightest torsion or other disturbance in the structure of the threads, which would be almost

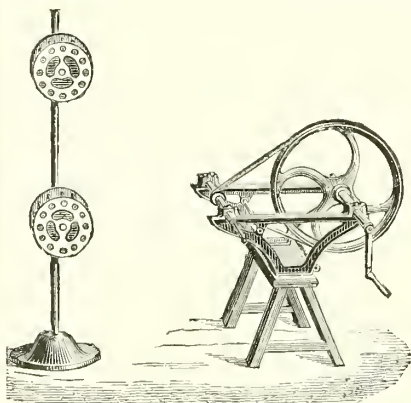


FIG. 3.

inevitable in any other process. The hanks, still slightly damp, are placed in a cupboard heated by steam, and finally hung up in an airy room until required. The amount of salt remaining in the fibre must, of course, be very small, but it is quite sufficient to influence materially the burning of the candle. The wick is next transferred to the spools, from which it passes to the machine. This task is performed by boys, who wind the wick off the hank previously stretched on a circular rotating frame, on to 'spools' or bobbins on spindles (fig. 3). As they wind, they let the wick run through their fingers, to detect any knots or other irregularities, which might interfere with the burning of the candle. The spools are now ready for transport to the machine. The old 'hand-frame,' the forerunner and nucleus of the present complicated apparatus, consists of a cluster of pewter moulds held together by wooden collars at either

end. Each mould is traversed longitudinally by a wick, which is secured by a peg at the top and wire at the base, and it has to be provided with a little loop of cotton, through which a wire is passed.

The butt-ends of the moulds open into a trough about two inches deep. Into this the hot material is poured until it is quite filled, and the whole frame is then placed in a tank of water, the temperature of which varies with the description of candle, as will be explained presently. When quite cold, the candles are removed from the pipes by simply inverting the frame, the cake of superfluous wax having been previously scraped off, and the wires and pegs withdrawn. As the pipes are made slightly conical, and as the substance shrinks in cooling, there is seldom any difficulty in emptying the frame; or if one or two of the candles should refuse to leave the moulds a slight tap with a mallet speedily loosens them. This method is obviously slow and cumbrous, and were it not that some people will have hand-made goods, also, that a few odd sizes for which it would not be worth while to keep special machines can only be made in hand-frames, there would not be a frame in a factory. A hand-frame can be filled and emptied, at quickest, once an hour, while a machine will do thrice the amount of work in the same time.

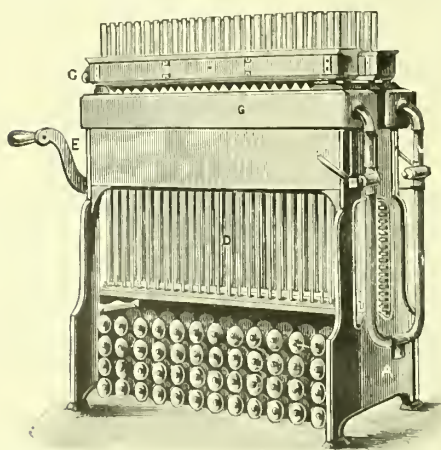


FIG. 4.

Fig. 4 represents a candle-machine of recent manufacture, for making candles with ordinary, *i.e.* not self-fitting, ends. It consists, mainly, of a metal tank (o) in which the pipes are fixed with their butts opening in a trough and their tips emerging below. The tips are not of one piece with the moulds, but can slide up and down, fitting water-tight when drawn home. The motion is communicated by pistons (v), to which the tips are soldered, and which are perforated longitudinally.

The wicks wound on the spools before-mentioned, which rotate on a series of spindles at the base of the machine, pass up these perforations D. The tanks G which surround the pipes are connected with hot and cold water cisterns, or preferably with cold water and steam.

To commence the operation the wicks are drawn through the pistons, tips, and pipes, and temporarily secured in the troughs. These, and the moulds opening into them, are now filled roughly, merely to afford a starting-point for the wick, and emptied as soon as the material is cold. To effect this the trough is scraped clear with a spud, after which the handle E is slowly turned. This by means of rack and pinion gear imparts a vertical motion to the pistons, which mount up the pipes, carrying the dummy candles with them, and unwinding the wick from the spools. As the candles emerge from the pipes they are received in a clamp frame C, which is held open by a spring handle. When the tips are clear of the trough the clamp is closed, gripping the candles firmly. The handle is now turned the reverse way, causing the pistons to descend in the moulds till the tips close the ends securely. Thus the wicks are left in the centre of the pipes, held by the dummies above and the spools below. The next step depends on the nature of the material used. If stearin candles are to be made the tanks are charged with tepid water, the temperature of which the operator determines by his hand in preference to other methods. The reason for this precaution depends upon the highly crystalline structure of stearic acid, which renders it liable to crack if chilled too suddenly, or to crystallise if cooled too slowly, whereby the appearance if not the structure of the candle would be impaired. On this account also the melted stearin is stirred while in the melting pans till it assumes the consistency and appearance of gruel, in which state it is transferred to the 'jacks,' and thence to the moulds. When these are full they are allowed to rest about twenty-five minutes until they are sufficiently hard to permit of their being withdrawn without fracture. The troughs are not scraped in this case, as the tops are hard enough to act as clamps if supported on side pieces. As soon as the pipes are filled again and the material set enough to hold the wick without extraneous aid, the upper row of candles, often whilst still hot, is removed into the air, where they cool and bleach. This tendency of stearin to crack was a great obstacle to the success of these candles when they were first introduced. Among the various devices employed to overcome the defect was that of stirring a small proportion of arsenic into the melted stearin. This certainly broke the grain, but it was of course diffused into the air on burning the candles. When this became generally known the prejudice against stearin was such as to affect the success of the new substitute for tallow, and to this day stearin candles enjoy but a comparatively limited popularity in this country.

Paraffin candles, on the other hand, are almost unknown on the Continent, whilst stearin is universally burnt; but when in 1854 James Young obtained from shale oil a pure white paraffin, which was subsequently made into candles under a patent of J. K. Field, the immediate popularity of the novel illuminant left little doubt as to what would be the material of the candle of the future. Still, even the most enthusiastic optimist of that day would have hesitated before accepting the prophecy which to-day has seen accomplished, that paraffin candles would be



sold at half the price of tallow dips, and that the costermonger would be able to illuminate his barrow and the driver his cab with a brighter light and drawn from a handsomer candle than was formerly within the rich man's reach.

The main difficulty experienced in beginning the manufacture of paraffin candles arose from want of precaution in regulating the temperature while casting. The same machine can be employed for either paraffin or stearin candles, but when paraffin is about to be used the water in the tanks is raised to a temperature of nearly 200° F., by passing steam through the pipe. Also the paraffin itself is heated to about 170°-180° F., and poured in a highly mobile state. When the pipes are filled the hot water is discharged from the tanks and cold water immediately introduced, thus suddenly chilling the fluid material. If the exact point be missed failure will result. Thus, if the pipes are colder than the inflowing paraffin it will congeal as it touches the metal, assuming a dull, striated aspect. On the other hand, if the moulds are suffered to cool slowly the candles will shrink on to instead of from the walls, and will be injured in extraction, if indeed they can be withdrawn at all without being melted out. When the operation is properly carried out, and the pipes are not worn with usage, and if, further, the paraffin is highly refined and of a high melting point, the candles leave the moulds with a lustre which hardly diminishes by ordinary handling. This lustre, combined with the translucency, snowy whiteness, and ready adaptability to ornament in shape and colour, gives paraffin the pre-eminence over all other materials for candle-making. It has, however, its disadvantages. The readiness with which it liquefies by heat gives a tendency to 'gutter' to even the best paraffin candles. Moreover, paraffins have the peculiar property, which is independent of their melting-points, of becoming plastic after exposure to a moderate degree of heat. The time required to develop this tendency varies, it is true, with the hardness or fusibility of the paraffin, which ranges from 105°F. to 140°F.; but even ozokerite, which is often wrought up to 112-3°F., is affected by protracted heat. The inferior varieties of these candles, from the ease with which their substance melts, are very prone to smoke; the wick is apt to be too abundantly supplied with fuel, and is consequently chilled below the point at which complete combustion can take place.

By judiciously mixing stearin and paraffin the candle-maker is able to obviate many of the defects of the substances whilst retaining their advantages. Such candles as petro-stearine, palmitine, and other popular varieties, are made on this principle.

One of the greatest improvements of the last quarter of a century in candle-making is the self-fitting end, by which simple device a candle will fit any normally constructed sconce without scraping or using paper, or other expedient to enlarge or diminish the butt. The self-fitting end, patented in 1864 by J. L. Field, is now in universal use. Fig. 5 will give an idea of the conical butt, while fig. 6 represents the machine patented by E. Cowles for its manufacture. The difficulty to be overcome lies in the butt projecting beyond the stem of the candle, which renders

the ordinary method of withdrawal impracticable. To meet this, the butts are cast in a separate frame, which can be fitted to or removed from the pipes at will. When the machine is to be filled the butt frame is lowered by the chain till the butts rest upon and fit tightly into their respective pipes. The wicks are then drawn through the butt moulds with a wire and clamped in a centric position, after which the filling is proceeded with in the usual manner. When cold the wicks are cast loose, the tops scraped off, and the upper frame hoisted off the butts as in the engraving, the operation being concluded as before. It will be noticed that this apparatus precludes running a continuous wick, as in the making of plain ends; and in a large factory a serious loss is incurred in the



Fig. 5.

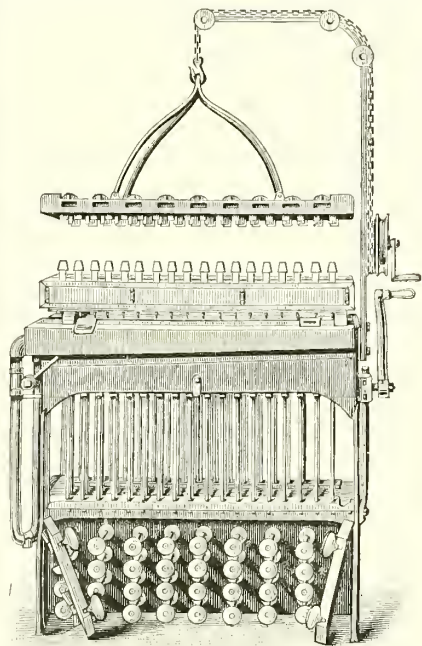


Fig. 6.

course of the year by the inch or two of wick snipped off at each operation. A very ingenious machine for saving this waste is also due to Mr. Cowles, who invented a split bed-plate holding the butts. When ready for withdrawal the butt moulds are raised and opened out by a simple lever motion, and the candles can thus be passed through without further trouble (figs. 7 and 8).

Another improvement, which has found more favour on the Continent than with us, consists in perforating the stem of the candle longitudinally so as to afford an internal escape for any grease which would otherwise have guttered down the outside. The up-draught of air which takes place in the tubes has a tendency to ensure more perfect combustion. By reason of the hardness required in their manufacture these candles must be made with stearin.



Much art has been expended on the ornamentation of candles. Before the introduction of aniline dyes, candles were coloured with such pigments as vermilion, ultramarine, and verdi-

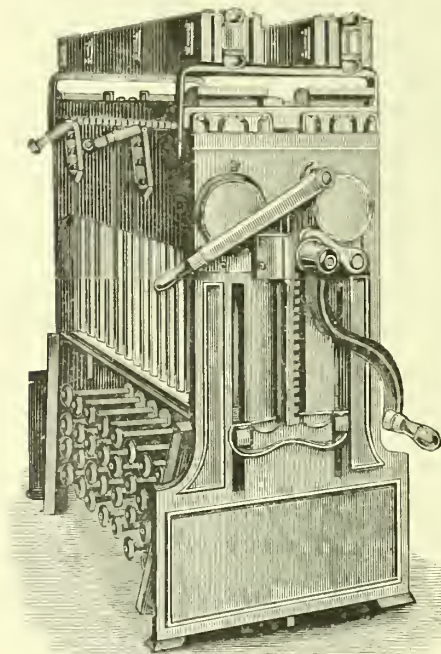


FIG. 7.

gris; these, besides causing a dull, heavy appearance, ruined the wick by choking it with incombustible matter. In wax candles this evil was minimised by confining the colour to the last

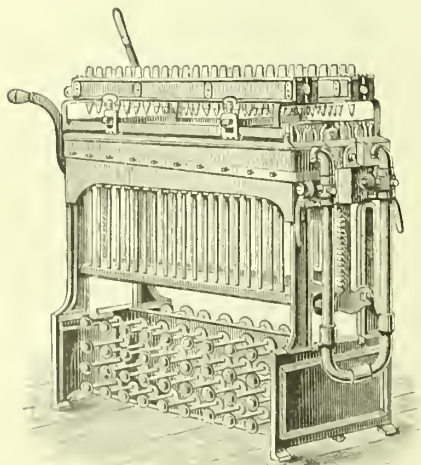


FIG. 8.

coating, which, owing to the opacity of the wax, gave the appearance of a candle coloured throughout with but slight effect on the burning. The

translucent paraffin, however, did not admit of this device. Paraffin candles are now coloured with the so-called coal-tar dyes by dissolving the dye in a small proportion of stearin, which, when added to the paraffin, colours it to any desired shade. Of ornamented candles (fig. 9), one of the most popular forms is the 'cable' or spiral



FIG. 9.

pattern. This form, as patented by Field, was made by turning the plain candle in a lathe of complicated structure, which could fashion over thirty different sizes and patterns of candles, *e.g.* cabled, spiral, fluted, striped, &c. By grooving out continuous patterns, replacing the candle in its mould, and running in coloured stearin, a number of fanciful devices were obtained, each of which had their period of popularity. The 'King Alfred's candle' where the stem is divided by grooves of this kind into sections burning an hour each, still enjoys favour.

The demand for cabled candles is now so large that they are made in moulds, the pistons while ascending being caused to rotate, so as to screw the candles out of their spiral moulds.

**Night lights** are short thick cylinders of some one or another of various fats and waxes, enclosed in paper cases and furnished with small wicks; their object being to give a constant and lasting rather than a bright light. They are usually cast direct in the cases, but of late, Price's Candle Co. have adopted the plan of casting the cylinders in a machine similar to a candle frame, and employing a material so hard (pressed cocoa-nut stearin) as to retain its form in hot weather without external support. These lights are burnt in glass cups, thus shedding their full light and rendering the precaution of water unnecessary. Another very popular form of this illuminator is Clark's 'pyramid' night-light, which, as its name indicates, is coniform. In this, the material employed is pressed tallow of great purity, and the wick is a rush-pith with two lateral strips of the peel left adhering. These turn outwards in burning, giving a neat and shapely flame. The base of the cone is a disc of plaster of Paris, which holds the wick upright till the whole of the fat is consumed; a result achieved less surely in the other kinds, where the wick is of 'inkle' (flax), held by a little strip of tin, into which the base of the wax fibre is fixed.

The strides made in gas and electric illumination have not materially affected the prosperity of candle manufactures. On the contrary, every year sees a considerable increase in the number

of candles made. The amount of paraffin worked up in Great Britain alone in the year 1887 could not have been much under 35,000 tons, judging from the outputs of the great Scotch companies. Price's Company turn out over 60,000,000 night-lights in a year, and other firms contribute their proportion, while stearin and other candles are made in immense quantities, one firm alone working about 2,000 tons of tallow annually.

L. F.

**CANDLE-NUT** is the fruit of the candleberry tree, *Aleurites triloba*, belonging to the family of spurge-worts or *Euphorbiaceæ*. The tree attains the height of 30 or 40 feet, and is a native of the Moluccas and South Pacific Isles, but is cultivated in many tropical countries. In India it is known as Indian akhrouit. The fruit of *A. triloba* is two-celled, fleshy, olive-coloured, and about two and a half inches in diameter. Each cell contains one nut resembling in appearance and taste a small walnut, the shell of which is very hard. The kernels having been dried are threaded on reeds, thus forming a candle; several of these candles being wrapped in a leaf of *pandanus* or screw-pine form a torch. The expressed oil of the candle-nut is known as eboc oil, country walnut oil, and artist's oil. It is palatable, but is chiefly used by painters as a drying oil. The Cingalese term it kekune, and the Sandwich Islanders kukui. It is said to be used by the latter as a mordant to their vegetable dyes. The refuse from the oil press is given to the cattle as food. It is imported into the British Isles, but only to a limited extent.

**CANELLA BARK.** The dried bark of *Canella alba*, obtained from Florida and the West Indies in large buff-coloured quills or pieces of about an inch broad. Has a bitter pungent acrid taste and odour of a mixture of cloves and cinnamon, due to a volatile oil containing *eugenic acid* which is also found in oil of cloves. The bark contains a bitter principle, *canellin*, together with resin, mannite, and starch. Used in medicine as an aromatic bitter and tonic, and in rheumatism and gout.

**CANELLE or BISMARCK BROWN** v. AZO-COLOURING MATTERS.

**CANNABIN or INDIAN HEMP RESIN** v. RESINS.

**CANNABINENE** v. RESINS.

**CANNABIS INDICA** v. RESINS.

**CANTHARIDES.** *Spanish flies* (*Cantharis vesicatoria*). Dried coleopterous insects used in medicine, in the form of plasters, tincture, liniments, &c., on account of their vesicating properties, due to a peculiar acrid principle, cantharidin.

Employed also as a stimulant diuretic, as an aphrodisiac, and as an emmenagogue. Obtained principally from Hungary, Russia, and the South of France.

**Cantharidin**  $C_{10}H_8O_4$  is obtained by treating the powdered insects with chloroform or ether, and evaporating the extract and treating the residue with carbon bisulphide to remove fat; or by mixing the cantharides with water and magnesia; drying, treating with dilute sulphuric acid, and extracting with ether. Crystallises in trimetric plates, melts at  $218^\circ$ , but begins to sublime at  $85^\circ$ . It is tasteless and inodorous; blisters the skin strongly, especially when in

solution or mixed with fat. Appears to be the lactone of cantharidic acid  $C_{10}H_{11}O_5$ , the alkaline salts of which may be obtained by heating cantharidin with aqueous solution of potash or soda.

**CANTON'S PHOSPHORUS** v. CALCIUM.

**CAOUTCHOUC** v. INDIARUBBER.

**CAOUTCHOUC OIL.** An oil which has proved efficient in preventing rust. It is spread with a piece of flannel in a very thin layer over the metallic surface which is to be preserved, and allowed to dry. To remove it, the article has simply to be treated with caoutchouc oil again, and washed after twelve to twenty-four hours (S. C. I. 1, 315).

**CAPSIUM RESIN** v. RESINS.

**CAPRIC ACID** or **DECOIC ACID** v. FATTY ACIDS.

**CAPROIC ACID** or **HEXOIC ACID** v. FATTY ACIDS.

**CAPRYLIC ACID** or **OCTOIC ACID** v. FATTY ACIDS.

**CAPSAICIN** v. RESINS.

**CAPUT MORTUUM.** A term employed by the alchemists to denote the residue remaining in the retort or alembic after the volatile matter had passed away.

**CARAGHEEN MOSS.** *Irish pearl moss* (*Chondrus crispus*); v. CARRAGEEN; ALGÆ.

**CARAJURU, CARCURU, or CRAJURU.** A Brazilian dyestuff of a red colour, said to be identical with *chica-red*, used by certain Indian tribes to stain their skins, and which is obtained from the leaves of the *Bignonia Chica*. It is a light, mealy, odourless, tasteless powder, which acquires a coppery lustre on trituration. Insoluble in water, but soluble in alcohol, ether, and alkalis (Virey, J. Ph. 1841, 151).

**CAREMEL.** The brown substance produced by the action of heat on sugar or glucose, and used for colouring liquors, sweetmeats, and gravies.

*Properties.*—Amorphous, dark brown, brittle mass; porous and deliquescent; completely soluble in water, partially soluble in alcohol; of a bitter taste and non-fermentable, but often contains unaltered sugar, which gives it a sweet taste and renders it fermentable. Melts at about  $100^\circ\text{C}$ .

*Preparation.*—Common sugar is heated, with constant stirring, in a metal pan capable of containing about ten times the quantity taken, till the whole mass melts, turns brown, and at last suddenly froths up, when the heat must be immediately stopped. During the heating much water and a little acid escape, but no permanent gas. Not more than 15 p.c. of the weight of the sugar should be driven off, as the product is liable to become insoluble if further heated.

For preparation of caramel colours, Asymus recommends the following processes (long kept secret):

*Colour for rum.*

Potassium or sodium hydrate . . . . .	3 kilos.
Water . . . . .	6 „
Or potassium or sodium carbonate . . . . .	4 „
Water . . . . .	8 „
Dissolve with heat in large iron pan, and add	
Glucose . . . . .	120 kilos.
Or syrup of glucose . . . . .	130 „

E E 2

Boil over the fire till irritating vapours begin to appear, then decrease the heat and stir continuously till the required shade is produced, then stop the process by adding 30 to 40 litres of water in a fine jet.

*Colour for beer or vinegar.*

Ammonium carbonate	. . .	6 kilos.
Water	. . .	6 "
Glucose	. . .	120 "

Process exactly as above.

*Detection of caramel in wines, &c.*—10 c.c. of the liquid to be tested is mixed with 30 to 50 c.c. of paraldehyde, and enough alcohol added to make the liquids mix; if caramel is present, it forms a dirty-brown precipitate sticking to the bottom of the vessel; the solution is poured off, the precipitate washed with alcohol dissolved in a little hot water, and the solution evaporated to 1 c.c., when different quantities of caramel may be compared by comparison of colours to confirm; this solution is mixed with one of 2 parts hydrochloride of phenylhydrazine in 20 of water, with excess of acetate of soda. Caramel yields an amorphous brown precipitate.

*Rough test for caramel in beer.*—Add a quantity of tannic acid, and shake thoroughly. If malt only is present, the colour is precipitated. Caramel colour remains unchanged.

Little is known of the chemistry of caramel. Gelis separated it into three amorphous substances, *caramelane*, *caramelene*, and *carameline*, differing in solubility and colouring power, but not of fixed composition.

**CARANNA** *v.* OLEO-RESINS.

**CARAPA BARK.** The bark of *Carapa Guianensis*, a miaceous tree found in Guiana and Hispaniola; has a bitter taste, and is used as febrifuge. Said to contain an alkaloid, *carapine* (Petroz and Robinet, J. Ph. 7, 293, 349).

The kernels of *C. Guianensis* yield by pressure a bitter fat oil, used by the Indians for protecting the skin against the punctures of insects (Cadet, J. Ph. 5, 49; Bouillay, J. Ph. 7, 293).

**CARBAMIC ACID**  $\text{CH}_3\text{NO}_2$  or  $\text{NH}_2\text{COOH}$ .

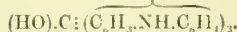
*Amidoformic acid.* An acid not known in the free state. *Ammonium carbamate* is, however, met with in freshly sublimed commercial ammonium carbonate, and may be prepared by mixing gaseous ammonia and carbon dioxide. Obtained also by the action of alkaline solution of potassium permanganate on albumen, leucine, tyrosine, and glycocoll.

**CARBAZOLE**  $\text{C}_{12}\text{H}_9\text{N}$  or  $\text{C}_6\text{H}_4\text{N} \cdot \text{C}_6\text{H}_5$ . A

white crystalline substance found amongst the products of the distillation of coal-tar, and occasionally met with in crude anthracene. May be obtained by passing vapour of aniline or diphenylamine through a red-hot tube, or by boiling imido-diphenyl sulphide  $\text{HN} \cdot \text{C}_6\text{H}_4 \cdot \text{S}$  with reduced copper. Forms white laminae, m.p.  $238^\circ$ , b.p.  $352^\circ$ .

By melting together carbazole and oxalic acid, and extracting with hot water and benzene, dissolving the residue in warm alcohol, filtering and evaporating, *carbazole blue* is obtained. The alcoholic solution of carbazole blue, when treated with glacial acetic acid and zinc-dust, is decolourised. Filtered into caustic soda solu-

tion the leuco-base separates out as a white flocculent precipitate. On oxidation with any of the usual reagents, the blue colouring matter is again formed. On the basis of this reaction, and on an analysis which, however, is not entirely satisfactory, Bamberger and Müller consider the compound to be a triphenylmethane derivative of the formula



(B. 20, 1,903, 1,907; S. C. I. 6, 660.) V. Dr. PHENYL.

**CARBODYNAMITE** *v.* EXPLOSIVES.

**CARBOHYDRATES.** (*Kohlenhydrate*, Ger.)

$\text{C}_n\text{H}_{2m}\text{O}_m$ ;  $n$ , as a rule, = 6 or some whole multiple thereof, and  $m=5$  or 6 or some whole multiple of them. A term applied to a large and important group of bodies forming *per se* the chief constituents of plants, and existing, but to a smaller extent, in animals and animal products; some of them are decomposition products of other organic compounds.

*Classification.*—There is no really satisfactory classification of these substances, our knowledge being at present not sufficiently extensive to admit of such; they may, however, be conveniently grouped as follows:

*Class I. Saccharans*,  $\text{C}_n\text{H}_{10}\text{O}_5$ . Amorphous, soluble in water, insoluble in alcohol: yielding directly bodies  $n\text{C}_6\text{H}_{12}\text{O}_6$  by the action of acids, no intermediate compounds being formed.

$\alpha$ -Amylan.	Levulan.
$\beta$ -Amylan.	Galactans $\alpha$ , $\beta$ , $\gamma$ and $\delta$ .
Dextran.	Paragalactan.

*Class II. Saccharens*,  $n\text{C}_{11}\text{H}_{18}\text{O}_5$ . Possessed of structure, insoluble in water and alcohol; yielding  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  compounds by the action of acids and certain ferments, and finally  $\text{C}_6\text{H}_{12}\text{O}_6$  by action of acids.

The Celluloses.	Starch.
Tunicin.	Inulin.

*Class III. Saccharins*,  $n\text{C}_6\text{H}_{10}\text{O}_5$ . Amorphous, soluble in water, insoluble in alcohol; yielding by the action of acids  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , and finally  $\text{C}_6\text{H}_{12}\text{O}_6$  bodies, converted by certain ferments into  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  bodies.

Maltodextrin.	Dextrin-like products
The Dextrins.	from Inulin.
Glycogen.	

*Class IV. Saccharoses.* The Sugars.

*Group a*,  $n\text{C}_6\text{H}_{12}\text{O}_{11}$ , *Saccharons*; sweet tasted; crystallisable, soluble in water and alcohol (not absolute); converted by acids and some by ferments into  $\text{C}_6\text{H}_{12}\text{O}_6$  bodies.

Sucrose (cane sugar).	Trehalose (Mycose).
Maltose.	Melezitose.
Lactose (milk sugar).	
Synanthrose (?).	
Mellitose (Raffinose).	

*Group b*,  $n\text{C}_6\text{H}_{14}\text{O}_6$ , *Glucoses*. Crystallisable, but with greater difficulty than members of group *a*; soluble in water and alcohol, broken down by the continuous action of acids, the products being no longer carbohydrates.

Fermentable by Yeast	Non-fermentable by Yeast
----------------------	--------------------------

Dextrose.	Sorbinose.
Levulose.	Crocase
Galactose.	Phlorose.
	Arabinose (?).

Identical with Dextrose,  
E. Fisher (B. 21, 988);  
Rennie (C. J. 1887, 636).



*Group c, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>.* Probably aromatic compounds having little or nothing in common with the other members of the carbohydrate group.

Inosite. † Identical, Maquenne Scyllit.

Dambose. † (C. R. 104, 1853-55).

*Class V. Compounds related to the carbohydrates and capable of yielding these substances by the action of acids, and some of them by that of certain ferments.*

Gums, mucilages, glucosides, pectins.

Tollens (Die Kohlenhydrate, Breslau, 1888) classifies the carbohydrates according to the number of C<sub>6</sub> groups contained in the molecule. Starting with bodies of the glucose type, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, he terms them *monosaccharides*, the saccharoses of the cane-sugar type, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, being *disaccharides*; raffinose, C<sub>18</sub>H<sub>32</sub>O<sub>16</sub>, or C<sub>3</sub>H<sub>6</sub>O<sub>22</sub>, would be a *trisaccharide* or *hexa-saccharide* according as the molecule contains three or six C<sub>6</sub> groups; Tollens places these compounds among the *polysaccharides*, the molecular weights of which are unknown, but which probably contain many C<sub>6</sub> groups.

Scheibler (B. 18, 646) has suggested a classification of the sugars which is also based upon the relative magnitude of the molecules; all sugars being described as saccharoses, Scheibler proposes to alter the termination of the word in such a manner as to indicate the size of the molecule. The simpler sugars, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, would be dextrose, levulose, galactose, &c., and sugars of the cane-sugar type, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, *saccharobiose*, *maltobiose*, *lactobiose*, while raffinose, C<sub>18</sub>H<sub>32</sub>O<sub>16</sub>, receives the syllable *tri* before the termination, making the word *raffinotriose*. This system has not hitherto found many adherents.

1. *General characters.*—All the members of the group, except those mentioned under Class IV. c, when submitted to the continued action of sulphuric or hydrochloric acid yield as final products brown or black humous substances, formic acid, and levulinic acid; this latter acid is aceto-propionic acid CH<sub>3</sub>.CO.CH<sub>2</sub>.COOH.

2. Certain unorganised ferments, produced usually during the process of germination (malt-*ing*, &c.), and acids convert some of the members of Class II. into those of Class III., and finally into those of Class IV.; this change is accompanied by the fixation of one or more water molecules.

3. The power of reducing solutions (chiefly alkaline) of the oxides of the heavy metals, such as those of gold, platinum, silver, mercury, copper, bismuth, &c., in some cases to metals, in others to lower oxides, is possessed by all the glucoses and by some of the saccharons, Class IV. a.

4. Solutions of all the carbohydrates possess the power of rotating the plane of polarisation of a ray of light (*i.e.* are optically active); some rotate to the right, some to the left, the intensity of the rotation varying with the substance, the strength of the solution, and the refrangibility of the ray, &c. (*v. SACCCHARIMETRY*).

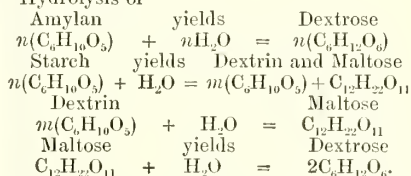
*Mutual relationships.*—The mutual relations of the members of the carbohydrate group are in many instances fairly apparent. The amylans are hydrated *directly* to dextrose by the action of acids; starch, on the contrary, yields the intermediate bodies, dextrin and maltose, which are finally converted into dextrose.

The final product of the action of acids on cellulose is also dextrose, but the relation of cellulose to the starch series is not understood. Dextran and levulan may be the saccharans of the suerose, or cane-sugar series, but bodies corresponding to starch and dextrin are at present wanting in this series.

Sucrose yields levulose and dextrose, and lactose or milk sugar, galactose and dextrose, and in this way other members of the group are related.

These changes may be expressed by the following equations:

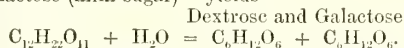
Hydrolysis of



Sucrose (cane-sugar) Dextrose and Levulose  
 $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$

Although this equation represents the generally received theory of the decomposition, there seems to be some doubt of its correctness (H. Winter, C. C. 1887, 1,373-1,374).

Lactose (milk-sugar) yields



In this case also it is highly probable the reaction is not so simple as it is represented by the equation.

Inulin yields a series of dextrin-like substances and finally levulose C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. The decomposition appears to be similar to that of starch (*v. supra*). See also Dragendorff (Materialien zu einer Monographie des Inulins, St. Petersburg, 1870); Honig and Schubert (Sitz. W. 96 [2] 653); and (M. 8, 529-560). The levulans (there may be two or more) hold probably the same relation to inulin as the amylans do to starch, and levulose takes the place of dextrose in this group. Some members of the inulin group are wanting, or are imperfectly known.

Lactose yields galactose and dextrose by the action of acids, but whether there are dextrin, starch, and amylan bodies of this set is not at present known. Galactans yielding galactose direct by the action of acids are probably the saccharans of the milk-sugar group. Most of the other members of the C<sub>12</sub>H<sub>22</sub>O<sub>11</sub> group yield dextrose on digestion with acids, but what relation the various members hold one to the other it is at present impossible to say.

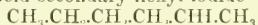
Fisher and Tafel (B. 20, 2,566) converted dextrose into levulose in the following manner. The phenylhydrazin compound with dextrose '*glucosazone*' C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>1</sub> when reduced with zinc and acetic acid yields isoglucosamin C<sub>6</sub>H<sub>13</sub>NO<sub>3</sub>, and this base reacts with nitrous acid with evolution of nitrogen and the production of a sugar identical in every respect with levulose.

A. J. Brown (C. J. 49, 172) indirectly performed the same, and the converse reaction. Dextrose is converted into mannitol by nascent hydrogen, and mannitol under the influence of *Bacterium aceti* yields levulose. Levulose in presence of growing *Bacterium xylinum* (C. J.

49, 432) is converted into cellulose, and cellulose into dextrose by acids.

The gums are acids, and yield, amongst other products, directly members of Class IV. group *b*, by the action of dilute mineral acids. Some of the mucilages are gums, others belong probably to Class I.

**Constitution.**—If we turn from these speculations to the consideration of the constitution of the carbo-hydrates, the facts as far as the glucoses are concerned are fairly clear. The first broad fact is that *alcohols* are formed amongst the products of the action of nascent hydrogen on these substances. Dextrose and levulose yield mannitol  $C_6H_{14}O_6$  under these circumstances, whilst galactose yields the isomeric alcohol, dulcitol  $C_6H_{12}O_6$ . It has been proved by Müntz and Aubin (C. R. 83, 1213) that the mannitols obtained from dextrose, levulose, and invert sugar are identical. Wanklyn and Erlenmeyer (J. 1861, 731, and 1862, 480) have shown that both mannitol and dulcitol yield secondary hexyl iodide



by the action of hydriodic acid; it is therefore evident that the glucoses from which these alcohols are formed must also possess all their six carbon atoms united in a normal chain.

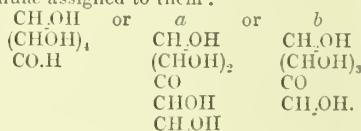
We do not think that sufficient stress has been laid upon the relative proportions of these alcohols obtainable from the glucoses; it is well known that much more mannitol is obtainable from levulose than from dextrose, and the proportion of dulcitol from galactose is greater than that of mannitol from either; further, the proportion in the most favoured case is far below the theoretical quantity. Other products are formed, and even in the most favoured case (dulcitol) in quantities quite as great as that of the alcohol. We should have some knowledge of these products before we build much upon the production of these alcohols from the glucoses, and we feel satisfied that the by-products are much greater than can be accounted for by the action of alkalis upon the sugars or on the resulting products. They may, however, be allied to the pinacones, double tertiary alcohols, produced by the action of nascent hydrogen upon the ketones.

According to the experiments of Berthelot (A. Ch. [3] 60, 93) the glucoses, at all events dextrose, when submitted to the action of acetic anhydride, yield a body which contains 5 acetyl groups for every 6 atoms of carbon, but the experiments are decidedly incomplete; if we admit the production of this compound we have no means of judging how the glucose molecule enters into the reaction. Colley (C. R. 70, 401) obtained a dextrose-monochlorhydrin-tetracetate  $C_6H_7O_4Cl(CH_3CO_2)_4$  by heating dextrose with five molecules of acetyl chloride. Other similar compounds have been obtained by the action of sulphuric, nitric, and many organic acids upon the glucoses; they are somewhat difficult to obtain in a pure state, but at all events they point to the pentahydric alcohol nature of these sugars.

Valuable evidence as to the constitution of the sugars is afforded by the products of their oxidation. Kiliani (A. 205, 192) has shown that levulose yields more than one third of its carbon in the form of *glycollic acid* on oxidation

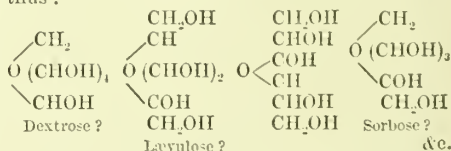
by means of silver oxide (other products of the reaction are carbonic, formic, and oxalic acids); hence he concludes that more than one  $CH_2OH$  group must exist in that sugar. The reducing power of levulose in alkaline metallic solutions, and the products of its oxidation by nitric acid, viz. glycollic acid  $CH_2HO.COOH$  and inactive tartaric acid  $(CO.OH)_2(CH_2HO)_2$ , make together a strong argument in favour of a ketone constitution for levulose (Kiliani, B. 14, 2530). Dextrose, on the other hand, yields by oxidation acids retaining all six carbon atoms, viz. gluconic acid,  $C_6H_{12}O_7$ , and saccharic acid,  $C_6H_{10}O_8$ , while galactose gives isomers of these, galactonic and mucic acids, hence dextrose and galactose cannot be ketones, and taking their reducing power into consideration, an aldehyde formula would be more probable.

From these facts it is inferred that the glucoses must have one or other of the following formulae assigned to them:



In the former we have the structure represented as mixed aldehydic and alcoholic, in the two latter as that of a ketone and an alcohol. Admitting the aldehydic structure, it is difficult to explain the isomerism of the glucoses; and further, these bodies do not possess two well-attested properties of the aldehydes, viz. they are not oxidised in the air, and they do not yield the beautiful violet-red colouration in a solution of magenta decolourised by sulphurous acid.

Tollens looks upon the glucoses as constructed thus:



As advantages of these formulæ, he points out the fact of the many possible variations, leaving room for the explanation of isomerism among the glucoses, the stability of the glucoses in the air, and their oxidation in the presence of alkaline metallic solutions such as those of copper, mercury, &c., supposing that in presence of alkalis they are immediately converted into aldehydes or ketones as the case may be.

Kiliani (B. 18, 3066) considers that levulose must be a ketone (this does not preclude Tollens' hypothesis), and determined that it has the formula *b* above given, and not *a*. Ketones combine with hydrocyanic acid, and the compounds so produced yield acids by the action of acids or alkalis. Levulose treated in this manner yields a hydroxyacid containing 7 carbon atoms, and this, when submitted to the action of hydriodic acid at high temperatures, yields an acid of the fatty series by the replacement of the hydroxyl groups by hydrogen. Now, if the formula of levulose is represented by the formula *b*, the fatty acid formed in this manner should be  $CH_3(CH_2)_4CH_2COOH$  methyl-butyl-

acetic acid, if by  $\alpha$ ,  $\text{CH}_3\text{CH}(\text{CH}_2)_2\text{CH}_2\text{COOH}$

ethyl-propyl-acetic acid. By preparing both these acids synthetically and comparing their properties with those of the acid obtained from levulose Kiliani found that the levulose body was methyl-butyl-acetic acid, and hence considered that the formula  $\beta$  above was the true formula of levulose. Confirmed by Bornstein and Herzfeld (B. 18, 3253) and Hönig (B. 19, 171) by oxidising levulose to formic acid, bioxy-butyric acid, and glycollic acid.

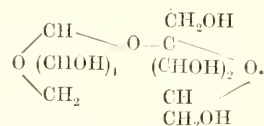
Kiliani (B. 19, 767, 1, 128) treating dextrose in the same way as he did levulose obtained normal heptylic acid, hence he concluded that dextrose has not the constitution of a ketone alcohol.

But little is known as to the constitution of galactose; it may possibly be a physical isomeride of dextrose. It differs from that substance in yielding dulcitol instead of mannitol by the action of nascent hydrogen; it has been already pointed out that dulcitol and mannitol both give secondary hexyl iodide on reduction by means of hydriodic acid, and yielding mucic acid  $\text{C}_6\text{H}_{10}\text{O}_8$  on oxidation with nitric acid instead of the isomeric saccharic acid. From the compound of galactose with hydrocyanic acid a well-crystallised hydroxyacid, galactose-carbonic acid  $\text{C}_6\text{H}_{10}\text{O}_8$  is obtained *isomeric* with dextrose carbonic acid, but converted by reduction into normal  $\gamma$ -oxyheptylic acid, and finally into normal heptylic acid, which are *identical* with the acids obtained in a similar manner from dextrose. Kiliani (B. 22, 915) and also Maquenne (C. R. 106, 286), Van 't Hoff and Lebel (Bl. 22, 237, Die Lagerung der Atome im Raume, Braunschweig, 1877) have occupied themselves more particularly with this question of physical isomerism. They have found that all compounds, without exception, which exhibit optical activity (rotation of the polarised ray) contain what they call *asymmetrical carbon*—that is, carbon in which all four affinities are satisfied by four *distinct* radicles; such a carbon atom is considered as lying in the centre of a tetrahedron, and each of the four different radicles with which it is combined at the four solid angles thereof. It is seen that *two modifications* of the compound are possible, which are related to one another like an object and its reflected image.

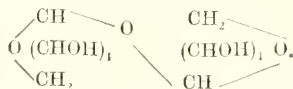
Taking the simplest formula applicable to the glucoses, the aldehyde formula, which on a plane surface shows no possibility of isomerism,

we see that it contains four asymmetrical carbon atoms, viz. those marked 2, 3, 4, and 5. The carbon atom 2 is combined with the four groups  $\text{CH}_2\text{O}$ ,  $\text{C}_4\text{H}_7\text{O}_7$ ,  $\text{OH}$ , and  $\text{H}$ ; carbon atom 3 is combined with  $\text{C}_3\text{H}_5\text{O}_6$ ,  $\text{C}_2\text{H}_3\text{O}_5$ ,  $\text{OH}$ , and  $\text{H}$ ; similarly with the carbon atoms marked 4 and 5; hence a large number of modifications are possible. Such substances would probably differ but little in their chemical relations, but show physical differences among which the optical variations are especially marked.

We have but little work to enable us to arrive at a conclusion as to how the glucose groups are arranged in the saccharoses. Tollens (B. 16, 921) expresses the opinion that cane-sugar is



Similarly maltose would be



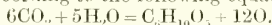
There can be no doubt that the molecule of starch, dextrans and celluloses, contains many  $\text{C}_6\text{H}_{10}\text{O}_5$  groups, but we have no evidence bearing on the arrangement of such groups in the molecule.

According to O'Sullivan's work (C. J. 1876, 1, 125; L.c. 35, 770), the starch molecule would appear to contain the  $\text{C}_6$  group at least twelve times, and Brown and Heron (C. J. 35, 596; and Brown and Morris, L.c. 47, 527) indicate that it would contain twenty such groups. It seems, however, probable that it is a  $\text{C}_{12}$  or maltose group which occurs in the starch molecule rather than a  $\text{C}_6$  group.

**Source.** The carbohydrates found in animals and animal products are derived from plants; dextrose of diabetic urine comes probably from starch. If it is yielded by sucrose it would be interesting to know what becomes of the levulose group. Is it converted into dextrose in the animal system? Starch and the celluloses may be the materials whence lactose of milk is derived, but inasmuch as there is an insufficiency of mucic acid-yielding bodies in the food-stuffs, it seems probable the saccharic-yielding group must in part be converted into the mucic acid-yielding one in the animal. Glycogen, too, has its origin in starch, and, indeed, possesses many properties in common with the higher dextrans.

The carbonic dioxide of the atmosphere is the material with which plants build up the carbohydrates; but upon this subject, too, our definite knowledge is very limited. There are, however, several hypotheses.

Sachs supposes that leaves, taking up carbon dioxide and giving up oxygen, build up starch according to the following equation



Boussingault and others consider that glucose is formed first. Von Baeyer (B. 3, 68) and Wurtz (B. 5, 534) look upon the formation of formaldehyde as the first step in the building up of the carbohydrates, carbonic acid being reduced; thus  $\text{H}_2\text{CO}_3 = \text{CH}_2\text{O} + \text{O}_2$ , the aldehyde then undergoing polymerisation.

According to the opinion of Liebig, carbonic acid is first transformed into formic and oxalic acids, and from these glycollic, tartaric, malic, &c. acids are built up, and these by further reduction yield glucose. This view is supported by Balls (B. 17, 6), and he considers that the carbonic acid supply is not derived directly from the atmosphere by the leaves, but from the soil in the form of acid carbonates by the roots.

When the carbohydrates are formed they are employed in building up the cellulose structure of the plant, and are stored up in the seeds, tubers, bulbs, &c. as a reserve to supply the first food to the young plant upon its start in



active life. During the early stages of the growth of seeds the carbohydrates, starch &c., are broken down, oxygen is absorbed (Day, C. J. 38, 645; Hellriegel, J. pr. 64, 94), carbon dioxide is evolved, and water formed. In some seeds the breaking down of the starch is accompanied at some stage by the formation of sucrose, maltose, &c. (Kjeldahl, M. C. L. 3; O'Sullivan, C. J. 49, 58).

The more important individual carbohydrates will be treated of under the name in its place according to the letter. The members of the sugar group will be found under the head 'Sugar.' O'S. and H.

### CARBOLIC ACID *Phenol* $C_6H_5.OH$ .

*Occurrence and formation.*—Carbolic acid occurs in small quantities in castoreum (Wöhler, A. 67, 360), in urine (Städeler, A. 77, 18), and is a constant product of the putrefaction of albumen (Baumann, B. 10, 685). It is formed when organic substances are strongly heated, and is contained in the tars obtained by the dry distillation of bones, wood (Duclos, A. 109, 136), shale (brown coal), and coal (Runge, P. 31, 69; 32, 308; Laurent, A. Ch. [3] 3, 195).

The tar produced in gas manufacture is the chief and almost exclusive source of carbolic acid. Owing to the demand for carbolic acid as a disinfectant and for the manufacture of dyes, it has become usual in tar distillation to collect a special fraction, the 'carbolic oil,' containing as much carbolic acid as possible, before collecting the 'creosote oil,' which contains the other phenolic constituents of coal-tar. The 'carbolic oil' begins to come over when the specific gravity of the distillate attains that of water. According to Watson Smith (C. J. 1886, 21), ordinary Lancashire coal-tar yields about 5 p.c. by volume of crude phenols containing 65 p.c. by volume of carbolic acid crystallisable at ordinary temperatures.

Coke ovens are now constructed so that the tar produced during the coking of coal can be collected; the following data having reference to the percentage of carbolic acid in such tars are given by Lunge (Coal Tar and Ammonia, ed. 1887). The tar from Hüssener's modification of the Carvès oven gave 1.37 p.c. of pure carbolic acid, the tar from the Simon-Carvès oven gave 0.05 p.c. of crude carbolic acid, and similar ovens working with another kind of coal and at a higher temperature gave 0.305 p.c. of crude acid. The tar collected from blast furnaces working with raw coal contains a high percentage of phenolic constituents, the quantity of carbolic acid present is, however, small (Watson Smith, *l.c.*).

Carbolic acid can be obtained by fusing potassium benzenesulphonate with caustic potash; the yield is proportional to the temperature and quantity of alkali employed, and is best (96.23 p.c. of that theoretically possible), when 1 mol. prop. of the former is fused with 6 mol. props. of the latter at 252°. Caustic soda cannot be employed instead of potash, since only a poor yield is obtained by its use (Degener, J. pr. [2] 17, 394).

*Preparation.*—Carbolic acid is almost exclusively obtained from coal-tar, and is worked up either from the special fraction known as 'carbolic oil' or from the oils intermediate in

specific gravity (sp.gr. = 1.000-1.020) between the light and heavy oils—oils, that is, distilling between 170° and 230°. The acid is also present in the creosote oils distilling between 240° and 270°, but it is not found practicable to separate it from this distillate with advantage. The first treatment of the oil consists in mixing it thoroughly in an iron vessel at a temperature of 40-50° with a quantity of soda ley (sp.gr. = 1.090-1.095) which has been determined by previous experiments on a small scale. Naphthalene and other hydrocarbons present in the oils are more soluble in strong than in weak soda ley, hence the importance of using the latter when the object is the preparation of pure crystalline carbolic acid; for crude acid, however, stronger ley up to a sp.gr. = 1.34 can be used with advantage. When no more carbolic acid is extracted from the oils—a point which is usually reached after about two hours' agitation of the mixture, and is ascertained by withdrawing from time to time portions of the liquor and testing the lower layer with acid, the liquor is allowed to clear and the lower layer consisting of carbolate of soda is drawn off from the oily upper layer which contains naphthalene and some of the higher homologues of benzene. The carbolate of soda solution (to which the soda ley washings obtained in the purification of the benzene and light oils produced in the distillation of coal-tar are added) is then treated with acid. Lunge, whose treatise on coal-tar and ammonia (ed. 1887) has been largely consulted for the purpose of this article, however, states that a previous purification is sometimes resorted to with the object of removing any dissolved or suspended hydrocarbons which would interfere with the crystallisation of the carbolic acid; for this purpose it is sufficient to pass a current of steam through the liquid (contained in an iron vessel provided with a condenser) until the distillate comes over clear and free from oil. The decomposition of the carbolate of soda is then effected in a lead-lined vessel by treatment either with hydrochloric, or more generally with sulphuric acid, until the reaction becomes distinctly acid. With hydrochloric acid there is no tendency for crystallisation to occur, and the liquor may stand for some time to ensure a complete separation of the carbolic acid, but when sulphuric acid is employed it is necessary to dilute it to sp.gr. = 1.70 (140°Tw.) to prevent immediate crystallisation of the resulting sodium sulphate, and to draw off the aqueous layer whilst still hot. To purify the crude carbolic acid so obtained many processes have been devised (*cf.* Bickerdike, C. N. 16, 188; Müller, Z. 1865, 270). That most usually followed is distillation of the acid in wrought-iron stills connected with zinc worms; water comes over first and the carbolic acid which distils over in the fractions 175-205° is either purified by a further distillation in a column apparatus or by repeated fractionation. The distillate so obtained should crystallise, but if this is not the case, distillation with a little potassium bichromate and sulphuric acid will yield a good, white, crystallisable product. It should be mentioned that carbolic acid frequently becomes coloured red on exposure to the air; a permanently white acid can, however, be obtained by completely oxidising

the substance producing the colouring matter, either by exposure to the air in shallow pans or by gently heating with potassium bichromate ( $\frac{1}{2}$  to  $\frac{1}{3}$  p.c.) and sulphuric acid previous to the final distillation. For very pure medicinal carbohc acid, one further distillation from glass vessels is necessary. (*Cf.* also, Ballard's Sanitary Report to the Local Government Board for 1878, 51; W. J. 1885, 465; Calvert, Z. 1865, 530; Behrens, D. P. J. 208, 363.)

*Properties.*—Carbohc acid crystallises in long, colourless needles, has a characteristic odour, melts at 42°, boils without decomposition at 182.3° at 760 mm. (Ladenburg, B. 7, 1687), at 183.3–184.1° (Adriezen, A. 6, 441), at 184° at 760 mm. (Lunge, Coal Tar and Ammonia, ed. 1887, 138), and has a sp.gr.=1.084 at 0° and =1.065 at 18° (Laurent). Ordinary 'pure' carbohc acid melts at 35° and boils at 188° (Lunge). The presence of small quantities of impurities such as water or naphthalene materially lowers the melting-point. The red colour of the ordinary commercial acid seems to be induced by the presence of minute traces of metals, particularly lead (Meyke, B. 16, 2513, *cf.* however, Ebell, B. 17, Referate, 69; Hager, B. 18, Referate, 114). Carbohc acid is a deliquescent substance, and in damp air forms a hydrate  $C_6H_5.OH + H_2O$  which melts at 17.2° (Allen, An. 3, 319); at the same time, however, it is not very readily soluble in water, 100 parts of water dissolving 4.83 parts at 11°, 5.36 parts at 35°, 6.19 parts at 45°, 7.33 parts at 58°, 11.83 parts at 77°, and at 84° both liquids mix in all proportions, whilst conversely 100 parts of phenol dissolve 23.3 parts of water at 9°, 26.75 parts at 32°, 31.99 parts at 53°, and 40.72 parts at 71° (Alexejeff, B. 10, 410). According to Hamberg (B. 4, 751), however, it dissolves in 15 parts of water at 16–17°. It is soluble in all proportions in alcohol, ether, benzene, glacial acetic acid, glycerine, olive oil, chloroform, carbon bisulphide, &c. The aqueous solution becomes coloured violet by ferric chloride and is without action on litmus. According to Kramers a mixture of benzene, toluene, xylene, naphthalene, anthracene acid, phenanthrene is obtained when the vapour of carbohc acid is passed through a red-hot tube (A. 189, 129). Two isomeric mononitrophenols are obtained by the action of dilute nitric acid (sp.gr.=1.34) (Fritzsche, A. 110, 150) and at lower temperatures the para- and at higher temperatures the ortho- derivative appear to be chiefly formed (Goldstein, B. 11, 1943). By the further action of nitric acid dinitrophenol (Kolbe, A. 147, 67) and trinitrophenol (picric acid) (Schmitt and Glutz, B. 2, 52) result. Chlorine (Laurent, A. 23, 60; 43, 209; Faust and Müller, A. 173, 303; Benedikt, M. 4, 233; Benedikt and Schmidt, M. 4, 606), and bromine (Körner, A. 137, 200, 205, 208, 209, 210; Hübner and Brenken, B. 6, 171) convert carbohc acid at the ordinary temperature into mono-, di-, and tri- substitution derivatives, and at higher temperatures or in the presence of halogen carriers such as antimony pentachloride &c. into tetra- and penta- derivatives. The nitro-, chloro-, and bromo- derivatives of carbohc acid are fairly strong acids, and the acid character increases with the number of nitro- groups or chlorine or bromine atoms introduced into the molecule. Iodine yields mono- and di- derivatives

in the presence of mercury (Hasiwetz and Weselsky, B. 2, 524) or iodic acid (Körner, A. 137, 213). Sulphuric acid converts carbohc acid into two isomeric monosulphonic acids (Kekulé, Z. [2] 3, 197) of which the ortho- acid is the chief product at the ordinary and the para- acid at higher temperatures. When heated with ammonium zinc chloride at 280–300°, carbohc acid yields aniline together with diphenylamine and phenyl ether (Merz and Weith, B. 13, 1299). When fused with caustic potash, salicylic acid, metahydroxy-benzoic acid, and two isomeric diphenols are formed (Barth and Schreder, B. 11, 1332) whilst fusion with caustic soda results in the formation of pyrocatechol (catechin) resorcinol (resorcin), and phloroglucin (phloroglucin) (B. 12, 417). The behaviour of sodium and potassium phenates (carbolates) when heated in a current of carbon dioxide has been studied by Kolbe (J. pr. [2] 10, 89; *cf.* also Schmitt, J. pr. [2] 31, 410; Germ. pat. 29,939, June 24, 1884); with sodium phenate the reaction commences below 100°, is most rapid and complete about 180°, and continues up to the temperature of the decomposition of sodium salicylate with the formation of that compound as sole product, but with potassium phenate salicylate is formed only at temperatures below 150°, whilst at higher temperatures the isomeric potassium parahydroxy-benzoate constitutes almost the entire product; in these reactions one half of the phenol is recovered. When carbohc acid is heated with phthalic anhydride and a dehydrating agent such as zinc chloride or sulphuric acid, it yields phenolphthalein (Baeyer, B. 9, 1230; A. 202, 68). If the acid is heated with oxalic acid and sulphuric acid it is converted into coralline (Zulkowsky, A. 194, 119; 202, 184), from which pure aurine can be extracted by suitable methods (Dale and Schorlemmer, A. 196, 77), whilst benzaurin results from heating carbohc acid with benzotrichloride (Doebner, B. 12, 1462).

*Reactions.*—1. In aqueous solution carbohc acid gives a violet colour with ferric chloride, this, however, is neither developed in very dilute solutions (Sarauw, B. 15, 46) nor in the presence of alcohol (Hesse, A. 182, 161); limit of sensitiveness, 1 in 2,000 (Polacci, B. 7, 360).—2. The aqueous solution on treatment with  $\frac{1}{4}$  vol. of ammonia and then with a few drops of an aqueous solution of bleaching powder (1 part in 20 parts of water) gives either at once or on standing a blue colouration; limit of sensitiveness, 1 in 4,000 (Salkowski, Fr. 11, 316).—3. Bromine water added to an aqueous solution of carbohc acid gives either at once or on standing a yellowish-white, flocculent precipitate of tribromophenol bromide (Landolt, B. 4, 770); limit of sensitiveness, 1 in 43,700 (*ibid.*), 1 in 80,000 (Lunge).—4. A solution of carbohc acid assumes a deep-red colour when boiled with  $\frac{1}{3}$  to  $\frac{1}{2}$  its bulk of Millon's reagent (a 10 to 15 p.c. solution of mercurous nitrate containing nitrous acid); limit of sensitiveness, reaction distinct with 1 in 60,000, and still appreciable with 1 in 200,000. Salicylic acid gives a similar reaction (Plugge, Fr. 11, 173; Almén, J. 1878, 1079).

*Quantitative estimation.*—Carbohc acid occurs in commerce in different qualities; as crude acid, as liquid acid, and as crystallised acid of

varying degrees of purity. (a) Testing of crude carbohc acid. 1. The percentage of phenols in crude carbohc acid can be approximately determined by shaking it with twice its volume of 10p.c. soda ley added gradually; the separation of the oily and aqueous layers becomes more accurate if a known quantity of petroleum spirit equal in volume to that of the layer of indifferent and resinous substances is added, and the amount added afterwards deducted. The phenols are estimated in a portion of the aqueous layer by treatment with hydrochloric acid and subsequent addition of salts to ensure a complete separation. Such a correction is, however, hardly called for, since the phenols will dissolve about as much water as the water will dissolve phenols (Beckurts, *Ar. Ph.* [3] 24, 572). Beckurts (*Ar. Ph.* [3] 24, 580) also states that Koppeschaar's method (*v. infra*) gives satisfactory results for testing liquid carbohc acid when the specimen is free from cresols. Casthelaz (*Bl.* 42, 574) tests measured samples of crude or liquid carbohc acid in tubes with water, with sulphuric acid (1 to 1), and with soda solution (1 part soda ley (sp.gr.=1.38) to 9 parts of water) and finally fractionates a fourth sample.

2. Testing of the pure acid. The exact quantitative estimation of carbohc acid is always made by precipitating it with bromine as tribromophenol bromide. The composition of this precipitate was believed to be tribromophenol (Landolt) until its true nature was ascertained by Benedikt (*cf.* Weinreb and Bondi, *M.* 6, 506). Koppeschaar's method (*Fr.* 15, 233) is the one usually employed, and this requires the following solutions: (a) solution of sodium thiosulphate (hyposulphite) equivalent to a solution of iodine containing 5 p.c. of iodine; (b) solution of starch; (c) bromine water (titrated with pure carbohc acid), or preferably a solution of bromine in caustic soda prepared by adding an excess of bromine to the soda and subsequently removing the excess either by boiling (Allen, *S. C. I.* 1884, 64), or by evaporating the solution to dryness and again dissolving in water; (d) solution of potassium iodide containing 125 grams in the litre. The process consists in treating 25 c.c. of the aqueous solution of carbohc acid (4 grams in the litre) with 100 c.c. either of the solution of bromate and bromide with 5 c.c. of concentrated hydrochloric acid to liberate the bromine, or of bromine water in a stoppered bottle, which is then well shaken, allowed to remain for fifteen minutes, then treated with 10 c.c. of potassium iodide solution, again shaken and finally titrated with the thiosulphate to determine the liberated iodine. The reactions involved are the following: 1.  $C_6H_5.OH + 4Br = C_6H_4.Br_3.OBr + 4HBr$ ; 2.  $C_6H_4.Br_3.OBr + 2KI = C_6H_4.Br_3.OK + 2KI + I_2$  (Weinreb and Bondi, *l.c.*); so that, as Beckurts points out (*l.c. infra*) the assumption made by Koppeschaar in the preceding method that 6 atom. props. of bromine enter into combination with 1 mol. prop. of phenol is in practice correct. Beckurts (*Ar. Ph.* [3] 24, 562) gives the following as the best mode of estimating carbohc acid. The solutions employed are (a)  $\frac{1}{10}$  normal potassium bromide (5.939 grams in the litre); (b) centinormal potassium bromate (1.666 grams in the litre); (c) potassium iodide solution contain-

ing 125 grams in the litre; (d) decinormal sodium thiosulphate (24.8 grams of  $Na_2S_2O_3 + 5H_2O$  in the litre). For the titration 25 to 30 c.c. of the phenol solution (1 in 1,000) are treated with 50 c.c. each of the potassium bromate and bromide solutions, shaken with 5 c.c. of concentrated sulphuric acid, allowed to remain fifteen minutes, treated with 10 c.c. of the potassium iodide solution, and finally titrated with thiosulphate to estimate the amount of iodine liberated. The calculation is simple: from the 50 c.c. each of bromate and bromide solution, 0.2392 gram of bromine is liberated by the sulphuric acid, and this is capable of converting 0.0469 gram of carbohc acid into tribromophenol; 1 c.c. of the decinormal thiosulphate is equivalent to 0.008 gram of bromine, a quantity capable of converting 0.00156 gram of carbohc acid into tribromophenol; multiplying now 0.00156 by the number of c.c. of thiosulphate used, and subtracting the product from 0.0469 gives the weight in grams of phenol in the quantity of solution originally taken. This process is accurate whenever solutions of pure carbohc acid, or mixtures from which the pure acid can be separated, are to be tested, but it fails in all cases (*e.g.* crude carbohc acid) when other phenols, particularly cresols, are also present. Methods for the estimation of carbohc acid have also been proposed by Waller (*C. N.* 43, 152), Degener (*J. pr.* 2, 17, 390), and Chancelon (*S. C. I.* 1882, 203), but these are inaccurate (Beckurts). A method has been devised by Allen for determining phenols in carbohc soap (*An.* 1886, 103).

*Uses.*—Carbohc acid has powerful antiseptic properties, and is used on the large scale as a disinfectant. Large quantities of carbohc acid are also employed in the manufacture of salicylic acid, whilst in the colour industry a considerable demand for the acid exists, inasmuch as it is the source of picric acid and coralline, and is used in the preparation of some azo- colours.

*Compounds with metals.*—Potassium phenate  $C_6H_5.OK$ , formed by dissolving potassium in carbohc acid (Hartmann, *J. pr.* [2] 16, 36), or by heating carbohc acid with caustic potash (Baumann, *B.* 10, 686), crystallises in slender white needles readily soluble in water, alcohol, and ether. Sodium phenate can be prepared by similar methods, and is used in the manufacture of salicylic acid. Compounds with barium (Laurent) and lead (Calvert, *Z.* 1865, 531) have also been described.

**CARBON.** Symbol C. At. wt. 12. Carbon occurs in nature in the free state, and very abundantly in combination, notably in the form of carbonates, and as an essential constituent of organic bodies. In the free state it is a solid, infusible, non-volatile substance, without taste or smell, exhibiting great diversity in the physical characteristics of its three allotropic forms, diamond, graphite, and charcoal.

The diamond up to the time of Bergmann was supposed to be a kind of rock-crystal, although Newton regarded it as probably an unctuous substance coagulated. It was shown to be combustible by the members of the Academy del Cimento in 1694, and Lavoisier proved that the sole product of its combustion was carbon dioxide. He had previously ascer-



tained that this gas was a compound of oxygen and an element to which he gave the name of *carbone*, contained in coal and wood. Graphite, as its synonyms, blacklead and plumbago (from the Italian *grafio piombino*—the writing lead) imply, was long considered to be a kind of lead, or as related to antimony; Scheele regarded it as a compound of iron and carbon; Kastner proved that it was essentially carbon.

*Manufacture of wood charcoal.*—The earliest plan of *coaling wood*, as the manufacture of charcoal was termed, and is still called, is carried on as follows. A piece of ground is levelled at some convenient spot in the forest, which is termed the 'hearth' or 'carth.' In the centre of this a thick pole or bundle of brushwood is placed, around which the wood is arranged, some of the pieces being laid horizontally and others set up at an inclination, or the wood may be placed altogether at any steep angle, sloping outwards from the centre to form a flattened cone, which when complete is usually called a heap; the object, whichever way the wood is placed, is to obtain a free circulation of air under the heap to communicate with the chimney in the centre, which is formed by then withdrawing the central pole or bundle

of brushwood. The large wood should, if convenient, be at the bottom of the heap, and the outside packed as close as possible; the heap is then covered with small brushwood, and afterwards with turf, or the material most impervious to air which can be conveniently obtained. A fire is lighted in the centre chimney, and by leaving openings in the outside covering at the bottom of the heap, the fire soon extends, and can be guided to any part by making temporary openings to admit the air. When the heap is sufficiently fired all the openings are closed, and lastly the chimney itself. The fire will always extend most rapidly on the side facing or towards the wind, and great care must be taken to watch and check this, by keeping the covering on that side in good order. The charcoal-burner must always be careful to spread the fire as evenly as possible through the heap, and after it is coaled to stop it down carefully; he can always accelerate the process in any part of the heap, if well built, by opening the outside to admit air freely, but if he finds this does not act, from any fault in setting the wood, he had better open a hole with a bar at the place required, and light a fire in the hole; this will soon communicate with the main fire in the

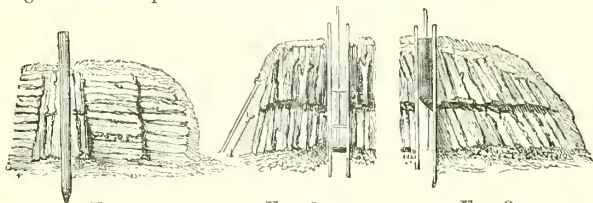


FIG. 1.

FIG. 2.

FIG. 3.

heap. As soon as the smoke and white flame cease to escape at the vents, the whole heap must be closed from the air as carefully as possible until the charcoal is quite cooled, and is ready to draw. The fire must never burn too fast; the slower the process, if the fire is steady and regular, the better the yield of charcoal. Hard close-grained woods take a longer time to coal than soft open-grained woods, and should be placed in the heap accordingly. These technical instructions, handed down in the forests for ages as secrets from father to son amongst the 'coaliers' in every country in Europe, are the results of long practical experience, and strictly accord with the true principles on which the process is based.

To carbonise wood under a movable covering, the plan of *Meiler*, or heaps, is employed very much in Germany. The wood is arranged either in horizontal layers, or in nearly vertical ones, with a slight slope, so as to form conical rounded heaps of different sizes. The former are called 'lying *Meiler*,' fig. 1, the latter 'standing *Meiler*,' figs. 2 and 3. Both are distributed in much the same way.

In districts where the wood can be transported into one place by means of rivers or mountain slides, a dry flat space must be pitched upon (screened from storms and floods), which may be walled round, having a slight declivity made in the ground towards the centre (v. fig. 4). Into this space the tarry acid will partially fall, and may be conducted outwards

through a covered gutter beneath into a covered tank. The mouth of the tank must be shut during the coking with an iron or stone slab, luted with clay. A square iron plate is placed over the inner orifice of the gutter to prevent it being choked with coal ashes.

Fig. 4 represents a walled *Meiler* station: *a* the station, *b* the gutter, *c* the tank, which is covered with the slab *d*; *e*, a slab which serves to keep the gutter clear of coals. The cover of the heaps is formed of earth, sand, ashes, or such other matter as may be most readily found in the woods. They should be kindled in the centre. From six days to four weeks may be required for charring a heap,

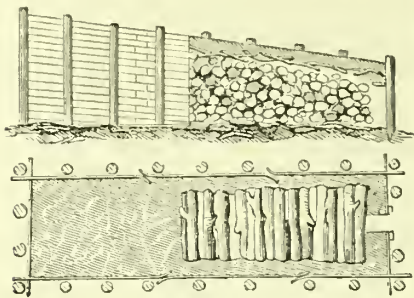


FIG. 4.

according to its size, hard wood requiring more time, and the slower the process the better and greater is the product, generally speaking.

Charring of wood in mounds (*Haufe* or *liegende Werke*) (figs. 5 and 6) differs from that in the *Meiler*, because the wood in the *Haufe* is successively charred, and the charcoal is raked out little by little. The product is said to be greater in this way, and also better. Uncleft billets, 6 or 8 feet long, being laid over each other, are covered with ashes, and then

carbonised. The station is sometimes horizontal and sometimes made to slope. The length may be 24 feet, the breadth 8 feet, and the wood is laid crosswise. Piles are set perpendicularly to support a roof made of boughs and leaves covered with ashes. Pipes are occasionally laid



FIGS. 5 and 6.

within the upper part of the mounds, which serve to catch and carry off some of the liquid.

Fig. 7 is a vertical section, and fig. 8 a half

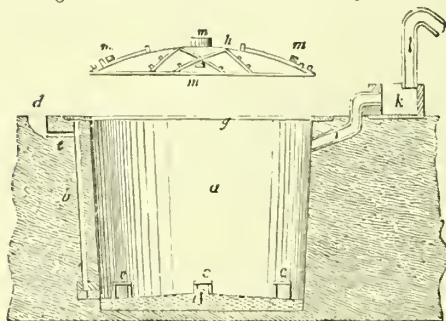


FIG. 7.

bird's-eye view and half cross-section at the height of the pit bottom, of Chabeaussière's kiln for making wood charcoal. *a* is the oven, *b* vertical air-pipes, *c* horizontal flues for ad-

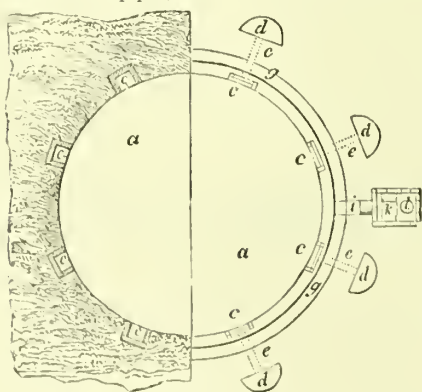


FIG. 8.

mitting air to the kilns, *dd* small pits which communicate by short horizontal pipes *ee* with the vertical ones, *f* the sole of the kiln, a circle of brickwork upon which the cover or hood *h*

reposes; *i* a pipe which leads to the cistern *k*, *l* the pipe destined for carrying off the gaseous matter, *mm* holes in the iron cover or lid.

The distribution of the wood is like that in the horizontal *Meiler* or heaps; it is kindled in the central vertical canal with burning fuel, and the lid is covered with a few inches of earth. At the beginning of the operation all the draught flues are left open, but they are progressively closed as occasion requires. In eight kilns of this kind 500 decasters of oak wood are carbonised, from which 15,000 hectolitres of charcoal are obtained, equal to 64,000 lbs. French, being about 25 p.c., besides tar and 3,000 vells of wood vinegar of from 2° to 3° Baumé.

At Crouy-upon-the-Oureq, near Meaux, there is a well-constructed kiln for making turf-charcoal. It resembles most nearly a tar-kiln. In fig. 9, *a* is the cylindrical coking place whose surrounding walls are heated by the flame which passes through the intermediate space *b*. The place itself is divided by partitions of fire tiles into three stages, through the apertures in which the flames of the fire, *cc*, rise, and heat the exterior of the coking apartment. In order to confine the heat, there is in the inclosing walls of the outer kiln a cylindrical hollow space *d*,

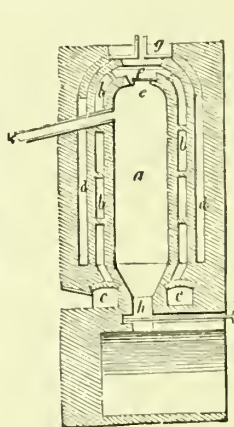


FIG. 9.

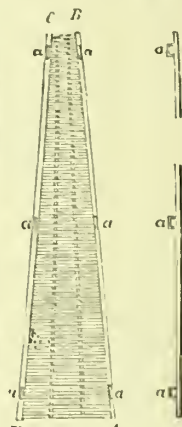


FIG. 10. FIG. 11.

where the air is kept stagnant. Through the apertures left in the upper end at *e*, the turf is introduced; they are then shut with an iron plate *f*, which is covered with ashes or sand. The fireplace opens above this aperture, and its outlet is provided with a movable iron cover *g*, in which there is a small hole for the issue of the gases. The sole of the kiln consists of a cast-iron slab *h*, which may be raised by means of a hook, *i*, upon it. This is drawn back after the carbonisation is completed, whereby the charcoal falls from the coking space into a subjacent vault. The volatile products are carried off by the pipe *k*, and led into the condensing cistern, the gases escaping to the fireplace, where they are burned. The iron slab is protected from the corrosion of the acid vapours by a layer of coal-ashes.

Charcoal obtained by the action of a rapid fire in close vessels is not so solid and so good a fuel as that which is made in the ancient way

by the slow calcination of pyramidal piles covered with earth. One of the most economical ovens for making wood charcoal is that invented by M. Foucauld, which he calls a shroud or *abri*. To construct one of these, 30 feet in diameter at the base, 10 feet at its summit, and from 8 to 9 feet high, he forms, with wood 2 inches square, a frame 12 feet long, 3 feet broad at one end, and 1 foot at the other.

The figures 10 and 11 will explain the construction. The uprights, *AB* and *CD*, of this frame are furnished with three pairs of wooden handles *aaa*, by means of which they can be joined together, by passing through two contiguous handles a wooden fork, the frame being previously provided with props, as shown in fig. 11, and covered with loam mixed with grass. A flat cover of 10 feet diameter, made of planks well joined, and secured by four cross-bars, is mounted with two trap doors, *MN*

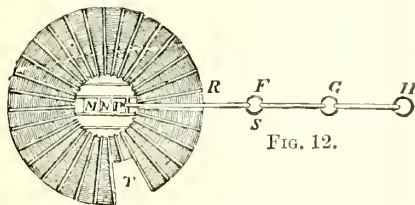


FIG. 12.

(fig. 12), for giving egress to the smoke at the commencement of the operation; a triangular hole *P*, cut out in the cover, receives the end of the conduit, *QRS* (figs. 13 and 12), of wood formed of three deals destined to convey the

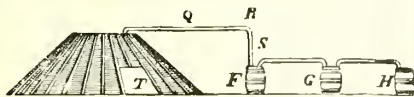


FIG. 13.

gases and condensed liquids into the casks *FGH*. Lastly, a door *T*, which may be opened and shut at pleasure, permits the operator to inspect the state of the fire. The charcoal calcined by this *abri* has been found of superior quality.

When it is wished to change the place where the *abri* is erected, and to transport it to a store of new-felled timber, the frame is taken down, after beating off the clay which covers it; the joints are then cut by a saw, as well as the ends of the fork which fixed the frames to one another. This process is economical in use and simple and cheap in construction, since all the pieces of the apparatus are easily moved about, and may be readily mounted in the forests. For obtaining a compact charcoal for the use of artisans this mixed process of Foucauld is said to be preferable to either the close iron cylinder or the pile.

For making gunpowder-charcoal the lighter woods, such as the willow, dogwood, and alder, answer best; and in their carbonisation care should be taken to let the vapours freely escape, especially towards the end of the operation, for when they are re-absorbed they greatly impair the combustibility of the charcoal.

The charcoal of some woods contains silica, and is therefore used for polishing metals. Being a bad conductor of heat, charcoal is

employed sometimes in powder to encase small furnaces and steam-pipes. It is not affected by water, and hence the extremities of stakes driven into moist ground are not liable to decomposition. In like manner casks when charred inside preserve water much better than common casks, because they furnish no soluble matter for fermentation or for food to animals.

For making crayons of charcoal the willow is the best wood that can be employed, as the softness is uniform in all its parts. The durability of charcoal may be seen in several of our old churchyards, where the letters made with lampblack are still perfect, though the whitelead with which the body of the stones was painted is entirely destroyed. This property of carbon is shown, however, in a more striking manner by the writings that were found in the ruins of Herculaneum, which have retained their original blackness for two thousand years. The ancients wrote with ink made from ground charcoal.

If it be required to purify any carbonaceous matter to render it fitter for delicate pigments, this may be done by first calcining it in a close vessel, and then lixiviating it in water slightly acidulated by nitric acid.

The incorruptibility of charcoal was well known to the ancients, and they availed themselves of this property upon all important occasions.

Some years ago a quantity of oak stakes were found in the bed of the Thames, in the very spot where Tacitus says that the Britons fixed a vast number of such stakes to prevent the passage of Julius Cæsar and his army. These stakes were charred to a considerable depth, had retained their form completely, and were firm at the heart.

Most of the houses in Venice stand upon piles of wood, which have all been previously charred for their preservation. In this country estates were formerly marked out by charred stakes driven to a considerable depth into the ground. These are occasionally found, and usually the charred portions are quite perfect, although every other part is decayed (Ure) (*v. WOOD, DESTRUCTIVE DISTILLATION OF*).

Wood charcoal possesses in a remarkable degree the power of absorbing gases in its pores, and in many cases of determining their combination. This power increases with its porosity. As ordinary charcoal contains atmospheric air in its pores, it must for this purpose be prepared by heating it to redness in a close vessel, and cooling over mercury. Saussure gives the following table for the absorptive power of freshly ignited boxwood charcoal upon different gases:

Ammonia gas . . .	90	vols.
Hydrochloric acid gas . . .	85	"
Sulphur dioxide . . .	65	"
Hydrosulphuric acid . . .	55	"
Nitrous oxide . . .	40	"
Carbon dioxide . . .	35	"
Ethylene . . .	35	"
Carbon monoxide . . .	9.42	"
Oxygen . . .	9.25	"
Nitrogen . . .	6.5	"
Hydrogen . . .	1.25	"

Charcoal obtained from the shell of the cocoa-nut appears to have still greater absorptive properties, absorbing according to Hunter,



Ammonia . . .	171.7 vols.
Carbon dioxide . . .	67.7 "
Carbon monoxide . . .	21.2 "
Oxygen . . .	17.9 "

In consequence of this absorption of gases in the pores of charcoal, their chemical activity is greatly increased. When a piece of charcoal which has absorbed a considerable quantity of sulphuretted hydrogen is introduced into oxygen, a violent reaction immediately takes place, water and sulphur dioxide being set free. If air be employed instead of oxygen, sulphur is deposited.

This property is utilised in the removal of fetid and bad-smelling gases from rooms, and in the sweetening of bad smelling liquids and of clothes. For this purpose charcoal of average porosity is found to be the most efficient, and it should be in moderate-sized pieces, its absorbent power being greater in this state than when in fine powder or in very large pieces.

Crude alcohol is occasionally allowed to remain for some time in contact with charcoal to remove fusel oil.

When charcoal is boiled in a solution of platinum tetrachloride, it becomes impregnated with platinum and is known as platinised charcoal. This substance possesses in a greatly increased degree the power of inducing chemical combination.

Charcoal containing 2 p.c. of platinum causes oxygen and hydrogen to unite completely in about a quarter of an hour, the rapidity increasing with the percentage of platinum, charcoal containing a larger quantity of platinum acting like platinum sponge. Platinised charcoal may be applied to the preparation of air-filters and respirators, and also as a mild caustic (Stenhouse, C. J. 8, 105).

A further property of charcoal is its power of depriving most coloured liquids of their colouring matters, by absorbing them within its pores. The colouring of red wine, cochineal, madder, or indigo, can thus be removed from solutions.

This property was discovered in 1700 by Lowitz, and is made use of on the large scale in several industrial operations, particularly in the process of refining sugar. It is most strikingly possessed by bone-black or animal charcoal (q. v.).

Charcoal of higher decolourising power is obtained from blood, horns, hoofs, clippings of hides, glue, &c., in contact with pearl-ash. A good decolourising charcoal is also obtained by carbonising vegetable matters mixed with chalk, calcined flints, or other earthy substances.

Charcoal also precipitates or absorbs certain substances from solution, notably iodine, lime and its salts (being used for the purification of highly calcareous waters), lead-salts and most metallic subsalts, besides many organic substances, as the bitter principles of hop, gentian, and aloe, tannin, alkaloids and resins, from their alcoholic solution.

**Gas-carbon** (*Glance coal*) is a very dense form of carbon, deposited in the upper part of the retorts in the manufacture of coal-gas and in blast-furnaces. It often exhibits the lustre and sonority of a metal, is very hard, and a good conductor of heat and electricity. It is used to form the negative element in a Bunsen battery.

**Lamp-black** is prepared on the large scale by burning fat, oil, resin, tar, &c., with an imperfect supply of air, either in a brick furnace or in cast-iron chambers, the products of combustion being conducted through a flue into a large chamber, from the ceiling of which a large cloth hood is suspended, upon which the lamp-black is deposited. In this way only the loose light soot is collected, the denser soot remaining behind in the flue.

An arrangement of lamps for the preparation of an especially fine quality of lamp-black from waste-fat and mineral oils is described in Payen-Paul, pp. 64, 65.

The lamp-black obtained by these processes contains about 80 p.c. of carbon, and is always contaminated with resinous and oily substances, together with water and ammonium sulphate, and small quantities of other inorganic salts. It can be purified by heating to redness in closed crucibles to remove organic matter, and by treatment with hydrochloric acid and subsequent washing with water to remove the mineral ingredients. Commercial lamp-black is, however, sufficiently pure for the purpose for which it is usually employed—viz., for painting and the manufacture of printer's ink.

#### COMPOUNDS OF CARBON.

**Carbon tetrabromide or Tetrabromomethane**  $\text{CBr}_4$ . White lustrous crystals, of a characteristic pungent smell, m.p.  $91^\circ$ , b.p.  $189.5^\circ$  (with slight decomposition). Insoluble in water, soluble in alcohol, ether, and chloroform. Best obtained by action of bromine on carbon disulphide in presence of iodine (Bolas & Groves, C. J. [2] 8, 161; 9, 773).

**Carbon tribromide or Hexabromide** *Tetrabromomethylene dibromide*  $\text{C}_2\text{Br}_6$ . Small rectangular prisms obtained by action of bromine on ethylene dibromide, or by heating  $\text{C}_2\text{H}_2\text{Br}_4$  with bromine and water at  $170^\circ$ . Soluble in carbon bisulphide; insoluble in alcohol and ether. Decomposed at  $200^\circ$  into  $\text{C}_2\text{Br}_4$  and  $\text{Br}_2$  (Rebout, A. 124, 271).

**Carbon ditribromide** *Tetrabromomethylene*  $\text{C}_2\text{Br}_4$ . White crystals, m.p.  $53^\circ$ , formed by action of nascent hydrogen on  $\text{C}_2\text{Br}_6$  (Löwig, A. 3, 292; Lennox, C. J. 14, 209).

**Carbon bromochloride** *v. WATTS' DICTIONARY.*

**Carbon tetrachloride or Tetrachloromethane**  $\text{CCl}_4$  was first obtained by Regnault (A. Ch. [2] 71, 337), who prepared it by the action of chlorine on chloroform in sunshine  $\text{CHCl}_3 + \text{Cl}_2 = \text{HCl} + \text{CCl}_4$ .

Dumas afterwards obtained it by the action of chlorine upon marsh gas (A. Ch. [3] 73, 95). It is now manufactured by passing carbon bisulphide saturated with chlorine through a red-hot tube. The mixture of carbon tetrachloride and sulphur chloride thus obtained is treated with potash or milk of lime and the tetrachloride distilled off (Kolbe, A. 45, 41; 51, 146). The tetrachloride may contain carbon disulphide if that substance was in excess or if the heat was insufficient. This may be removed by leaving the liquid for some time in contact with potash. Genthner removes the carbon sulphide by converting it into potassium xanthate by dissolving the mixture in alcohol, adding alcoholic potash so long as the liquid becomes

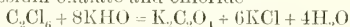
darker in colour, and heating gently; the unaltered tetrachloride is separated by water and purified by washing (Geuther, A. 107, 212).

Carbon tetrachloride may also be obtained by the action of antimony pentachloride upon carbon disulphide. The mixture becomes hot, and on cooling deposits crystals of antimony trichloride mixed with sulphur, whilst carbon tetrachloride remains in solution (Hofmann, C. J. 13, 65). Carbon tetrachloride is a thin transparent colourless oil, with a pungent aromatic odour; b.p.  $76.7^{\circ}$ , and sp.gr.  $1.63195_{25}^{20}$  (Thorpe, C. J. 1880, 201). It is insoluble in water, but soluble in alcohol and ether. It yields chlorine and lower chlorides of carbon on passing through a red-hot tube (Regnault, *L.c.*). When mixed with hydrogen and passed through a red-hot tube with pumice, it yields marsh gas and ethylene (Berthelot, A. Ch. 53, 69). Treated in the same manner with sulphuretted hydrogen it yields hydrochloric acid and carbon sulphochloride  $\text{CSCl}_2$  (Kolbe, A. 45, 41, and 54, 146). In alcoholic solution, and treated with potassium amalgam, it yields chloroform, marsh gas, and methene chloride (Regnault, *L.c.*). With phosphorus pentoxide phosgene is produced (Gustavson, Z. [2] 7, 615). With zinc and dilute acid it is converted into hydrochloric acid and chloroform (Geuther, *L.c.*). Alcoholic potash slowly converts it into potassium chloride and carbonate (Regnault, *L.c.*) by long-continued action at  $100^{\circ}$  in sealed tubes. Alcoholic potash converts it partially into ethylene (Berthelot, A. Ch. 109, 118). With phenylamine it yields carbtriphenyltriamine (Hofmann, Pr. 9, 284, and 10, 184). It is decomposed at  $200^{\circ}$  by molecular silver, being converted into hexachloroethane  $\text{C}_2\text{Cl}_6$  (Goldschmidt, B. 14, 927). By heating with aluminium bromide it is readily converted into carbon tetrabromide (Gustavson, Bl. [2] 36, 556).

**Carbon trichloride** *Carbon hexachloride, Tetrachlorethylene dichloride*  $\text{C}_2\text{Cl}_4$ , discovered by Faraday (Tr. 1826 47), also investigated by Regnault (A. Ch. [2] 69, 166, and [2] 81, 371) is obtained by the action of chlorine in sunshine upon various derivatives of ethyl and ethylene; on carbon dichloride, on ethylene chloride (Faraday, *L.c.*, and also Liebig, A. 1, 219); on ethyl chloride, first in the shade, afterwards in sunshine (Laurent, A. Ch. [2] 84, 328); on mono-, di-, or trichlorinated ethyl chloride (Regnault, *L.c.*); on ethyl sulphite (Ebelmen and Bouquet, A. Ch. [3] 17, 66); on ethyl oxide (Regnault); on hydrochlorate of ethylamine (Geuther and Hofacker, A. Ch. 108, 51) (in this process some chloride of nitrogen is produced); by passing the tetrachloride through a red-hot tube (Regnault, A. Ch. [2] 71, 737); by distilling perchlorethylidic oxide, and repeatedly treating the distillate with water (Malaguti, A. Ch. [3] 16, 6, and 14).

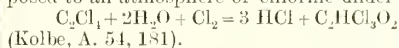
Carbon trichloride crystallises in right rhombic prisms. Colourless, transparent, and nearly tasteless, but having an aromatic odour. Sp.gr. =  $2.0$ ; m.p.  $187^{\circ}$ , volatilising even at ordinary temperatures. Insoluble in water, soluble in alcohol and ether, and in all oils. Converted by repeated distillation into the dichloride and free chlorine. Burns with a red light in the flame of a spirit lamp. Mixed with hydrogen

and passed through a red-hot tube it yields dichloride and hydrochloric acid (Geuther, *L.c.*). Metals heated in its vapour form metallic chlorides, charcoal being deposited. Heated with an alcoholic solution of potassium sulphhydrate it decomposes, yielding amongst other products carbon dichloride (Regnault, *L.c.*). Heated in sealed tubes with potassium hydrate it yields potassium oxalate and chloride



(Geuther, A. 60, 247). The same products together with hydrogen and ethylene are formed when it is heated with alcoholic potash in sealed tubes (Berthelot, A. Ch. 109, 118).

**Carbon dichloride** *Tetrachlorethylene*  $\text{C}_2\text{Cl}_4$  (Faraday, Tr. 1821, 47; Regnault, A. Ch. [2] 70, 104 and 81, 372), is formed as a liquid coloured with chlorine when the vapour of carbon trichloride is passed through a red-hot tube filled with fragments of glass. It is purified by passing it repeatedly through a red-hot tube, then shaking up with mercury and rectifying at a low temperature (Faraday). More easily obtained by adding carbon trichloride in small portions to an alcoholic solution of hydrogen potassium sulphide, as long as sulphuretted hydrogen is given off. The liquid is distilled and carbon dichloride separates from the distillate on dilution with water (Regnault, *L.c.*). Mobile liquid of sp.gr. =  $1.619$  at  $20^{\circ}$  (Regnault),  $1.612$  at  $10^{\circ}$  (Geuther), b.p. =  $122^{\circ}\text{C}$ . (Regnault),  $116^{\circ}\text{C}$ . (Geuther), remains liquid at  $-15^{\circ}$  and does not conduct electricity. Insoluble in water, acids, and alkalis, but dissolves in alcohol, ether, and oils. Decomposed at a red heat into the *hexachlorobenzene*  $\text{C}_6\text{Cl}_6$ , and free chlorine. When its vapour is passed over baryta at a red heat, it is decomposed with vivid ignition into barium chloride, carbon dioxide, and charcoal. It absorbs bromine in the sunshine, forming *carbon chlorobromide*  $\text{C}_2\text{Cl}_3\text{Br}$ . It is converted by continued heating to  $200^{\circ}$  with potassium hydrate into potassium oxalate and chloride, hydrogen being given off (Geuther, A. 110, 247). It absorbs dry chlorine in sunshine, forming the trichloride, but is converted into *trichloroacetic acid* when exposed to an atmosphere of chlorine under water



(Kolbe, A. 54, 181). **Hexachlorobenzene**  $\text{C}_6\text{Cl}_6$ , discovered in 1821 by Julien and investigated by Phillips and Faraday, Tr. 1821, and by Regnault (A. Ch. [2] 70, 144) who prepared it by passing the vapour of chloroform or tetrachlorethylene through a porcelain tube filled with fragments of porcelain and heated to redness; the crystalline product is dissolved in ether, filtered, evaporated to dryness and sublimed. Obtained by Hugo Müller as a final product of the action of antimony pentachloride or chlorine in presence of iodine on benzene. For other methods of preparation *v.* WATTS' DICTIONARY. Forms white delicate needles with a silky lustre, tasteless, but with an odour resembling spermaceti; sublimes without fusion at  $120^{\circ}$ .

Insoluble in water, acids and alkalis, but soluble in alcohol, ether, and hot oil of turpentine. Decomposed into chlorine and charcoal on passing through a red-hot porcelain tube filled with glass or rock crystal. Burns with a bluish colour in the flame. Potassium burns on being

strongly heated in its vapour. Formerly regarded as carbon monochloride: molecular formula established by Bassett (C. J. [2] 5, 443).

**Carbon tetraiodide** *Tetraiodomethane*  $\text{Cl}_4$ . Dark red octahedra; sp.gr. 4.32, obtained by action of aluminium iodide on a mixture of carbon tetrachloride and bisulphide (Gustavson, B. 14, 1705).

**Carbon nitride** *v. Cyanogen*, art. CYANIDES.

**Carbon oxychloride**  $\text{COCl}_2$ . *Carbonyl dichloride*, *Chloro-carbonic acid*, *Phosgene gas*. First obtained by J. Davy by action of sunlight on mixture of carbon monoxide and chlorine. For details of this mode of preparing it *v. Emmeling* & *Lengyel*, A. Suppl. 7, 101, and *Wilm and Wischin*, A. 147, 450. Also obtained by passing carbon monoxide into boiling antimony pentachloride (*Hofmann*, A. 70, 139; *Butlerow*, Z. 1863, 484; *Kraut*, Gm.-K. I. 2, 380); by heating carbon tetrachloride with zinc oxide in closed tubes at  $200^\circ$ , or by mutual action of carbon tetrachloride and carbon monoxide at  $400^\circ$ ; or by heating a mixture of chloroform, potassium bichromate, and sulphuric acid. For other methods *v. Watts' DICTIONARY*.

Carbon oxychloride is a colourless liquid boiling at  $8^\circ.2$ , and of sp.gr.  $1.432_{10}^\circ$ . Soluble in acetic acid and benzene; decomposed by water:  $\text{COCl}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl}$ . With alcohol forms *chlorocarbanic ether*  $\text{CO.CHO.C}_2\text{H}_5$ . Combines with ammonia to form *urea* and ammonium chloride.

**Carbon monoxide**; *carbonous* or *carbonic oxide*; *formic anhydride*;  $\text{CO}$ . Sp.gr. .9678 (air = 1). V.D. 14. ( $-186^\circ$ ) (*Wroblewski*, C. R. 98, 982). S.H.p. .2346. S.H.v. .16844 (*Wiedemann*, P. 157, 1). C.E. .003667 (*Regnault*). S. ( $6^\circ$ ) .0287; ( $9^\circ$ ) .0269; ( $18.5^\circ$ ) .02315 (*Bunsen*). S. alcohol ( $2^\circ$ ) .20356; ( $13^\circ$ ) .20416; ( $16^\circ$ ) .20566; ( $24^\circ$ ) .20452 (*Bunsen*);  $\mu_c = 1.000301$ ;  $\mu_k = 1.00035$ ;  $\mu_a = 1.000391$  (*Croullebois*, A. Ch. [4] 20, 136). Does not exactly obey Boyle's

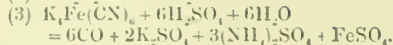
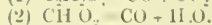
law;  $\frac{PV}{P_1V_1} = 1.00293$  (*Regnault*, Acad. 62, 26)

liquefied by cooling to  $-136^\circ$  at pressure of 200–300 atmospheres (*Wroblewski* and *Olszewski*, A. Ch. [6] 1, 112).

Discovered by *Lassonne*, and independently by *Priestley*. Composition first established by *Clement* and *Desormes*.

Produced by the oxidation of charcoal at high temperatures. By the deoxidation of carbon dioxide by means of hydrogen, carbon, metals, &c., at a red heat. In the reduction of metallic oxides by charcoal or coke. By the dry distillation of many organic compounds, and together with hydrogen and carbon dioxide when steam is passed over red-hot charcoal. By passing electric sparks through carbon dioxide (*Buff and Hofmann*, A. 113, 110) or by heating carbon dioxide to  $1,300^\circ$  (*Deville*, C. R. 59, 873). By heating dehydrated oxalic acid, or by heating dry alkaline formates and acetates with formic acid (*Lorin*, C. R. 82, 750). By heating an oxalate or formate or these acids with concentrated sulphuric acid.

Prepared by the decomposition of oxalic or formic acid or potassium ferrocyanide by concentrated sulphuric acid (*Fownes*).

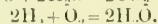
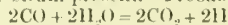


In the first case the gas is mixed with carbon dioxide, which must be removed by passing through potash or lime-water. In the last reaction it is quite free from carbon dioxide, but if the temperature is too high, a quantity of sulphur dioxide is produced in addition to the carbon monoxide. It is liable also to contain a small quantity of hydrocyanic acid vapour.

Dry calcium oxalate or barium oxalate is mixed with about  $\frac{1}{10}$  dry lime and strongly heated, the gas passed through lime and dried:  $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$ , any carbon dioxide formed being absorbed by the lime.

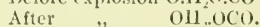
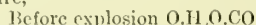
**Properties.**—Colourless, tasteless gas, combustible, non-supporter of combustion. Absorbed by carbon, by several metals, and by a solution of cuprous chloride in hydrochloric acid or ammonia. It acts as an energetic reducer. It is a highly poisonous gas, producing giddiness, and ultimately asphyxia when inhaled. According to *Leblanc* (A. Ch. [3] 5, 223), it is chiefly the presence of this gas that causes the poisonous action of air in which charcoal has been burnt. It combines with the red colouring matter of the blood-forming carboxyhaemoglobin, and may be recognised by its absorption spectrum, which is almost identical with that of oxygenated blood, and is characterised by two bands between D and E. On the addition of ammonium sulphide these disappear in the case of oxygenated blood, and the spectrum shows one band midway between D and E, but remain unchanged if carbon monoxide is present (*Vogel*, B. 11, 235; *Hoppe-Seyler*, Fr. 3, 439, also *Preyer*, J. 1867, 802; *Nawrocki*, J. 16, 640; *Gréhaud*, C. R. 87, 193). Carbon monoxide burns ordinarily with a blue flame, which by previous heating becomes red, generating carbon dioxide. The temperature of its flame in air is about  $1,400^\circ$  (*Valerius*, J. 1874, 58). When dry it is not changed by the electric current nor by ignited platinum wire, but when standing over water it is decomposed by a glowing platinum spiral (*Buff* and *Hofmann*, C. J. 12, 273). When not absolutely dry it may be exploded with oxygen by the electric spark or by platinum wire heated to  $300^\circ$  or by spongy platinum at ordinary temperatures. 2 vols. CO unite with 1 vol. O, forming 2 vols.  $\text{CO}_2$ .

*Dixon* (T. 1884, 617) has shown that no action takes place when a spark is passed into a mixture of perfectly dry carbon monoxide and oxygen, but that a mere trace of moisture renders the mixture explosive. The combination takes place very slowly in presence of small quantities of steam, and increases in rapidity with the quantity of steam present. Probable reactions:



Hence the steam acts as a carrier of oxygen to carbon monoxide (*v. Dixon*, C. J. 49, 94).

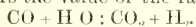
According to *Armstrong* (C. J. 49, 112), the changes are,



Small quantities of other gases than steam were tried: if the gas contained hydrogen, explosion occurred, if the gas contained no hydro-



gen, no explosion occurred. When a mixture of carbon monoxide and steam is heated to about 600° a portion of the carbon monoxide is oxidised. If the carbon dioxide is removed as it is formed, the whole may be oxidised. L. Meyer's experiments (B. 19, 1,099) seem to prove that a dry mixture of carbon monoxide and oxygen can be exploded if a very strong spark is used, and a sufficiently high temperature then obtained, and if the gases are under considerable pressure. When sparks from an induction coil are passed through a mixture of carbon monoxide and steam, carbon dioxide, a little formic acid, and sometimes carbon, are formed (Dixon, C. J. 49, 94). When to a mixture of dry carbon and hydrogen oxygen insufficient for complete combustion is added, and the mixture exploded by the spark, carbon dioxide and steam are formed in a ratio dependent upon the shape of the vessel and the pressure up to a certain limit, called the 'critical pressure.' Above this pressure the ratio of the formation of carbon dioxide and water is independent of the shape of the vessel. The critical pressure becomes lower the larger the quantity of oxygen used. The ratio  $\text{CO} + \text{H}_2\text{O} : \text{CO}_2 + \text{H}_2$  remains constant as long as the vol. of the hydrogen is more than twice that of the oxygen, provided no steam condense, and the pressure is above the critical pressure. When the vol. of hydrogen is less than twice the vol. of oxygen the above ratio diminishes. The presence of an inert gas increases the formation of carbon dioxide and diminishes that of water, hence it lowers the value of the ratio



This ratio is called the 'coefficient of affinity' of the reaction (Dixon, T. 1884, 617; C. J. 49, 94). According to Brodie, when carbon monoxide and hydrogen are submitted to the action of the silent discharge marsh gas is formed by synthesis, when pure and dry carbon monoxide is circulated through the induction-tube it is decomposed, carbon dioxide being formed together with other 'oxy-carbons' of the formulæ  $\text{C}_2\text{O}_3$  and  $\text{C}_3\text{O}_4$  (Brodie, Pr. 21, 245).

Carbon monoxide is converted into carbon dioxide under the influence of nascent oxygen from chromic acid (Ludwig, A. 142, 47), but not by ozone, either by diffused daylight or in direct sunshine (Remsen and Southwark, Am. S. [3] 11, 136). It is likewise oxidised by palladium charged with hydrogen in presence of oxygen and water (Traube, B. 15, 2325, 2854; 16, 123) (Remsen and Keiser, B. 17, 83) by mixing with oxygen and passing over platinum-black; by nitric oxide (Hasenbach, J. pr. [2] 4, 1) by heating with metallic oxides and with many oxysalts.

Pure carbon monoxide forms a colourless transparent liquid under 200-300 atmospheres at -139° and solidifies to a snowy mass in vacuo at -211° (Olszewski, C. R. 99, 706; 100, 350).

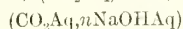
Carbon monoxide combines with potassium at about 80° to form an explosive compound,  $\text{KCO}$  (Brodie, C. J. [2] 12, 269). It is rapidly absorbed by a solution of cuprous chloride in ammonia or hydrochloric acid, by which means it may be directly estimated in a gaseous mixture (cf. Thomas, C. N. 37, 6). It unites directly with chlorine, forming phosgene gas (Schützenberger, Z. [2] 4, 321). It is absorbed by heated potassium hydrate at about 200°, forming potassium formate

(Berthelot, A. Ch. [3] 61, 463). Fröhlich and Geuther (A. 202, 317) recommend passing carbon monoxide over soda-lime for this purpose. It combines with sulphur to form carbon oxysulphide; with platinum tetrachloride to form  $\text{C}_2\text{O}_3\text{PtCl}_4$  and  $\text{C}_2\text{O}_2\text{PtCl}_4$  (Schützenberger, A. Ch. [4] 21, 430). It is rapidly absorbed by anhydrous hydrocyanic acid, cooled by a freezing mixture, two layers being formed, but the gas is evolved on removing the tube from the mixture (Böttlinger, B. 10, 1,122). It acts on metallic alcoholates with formation of acids by synthesis (Geuther, A. 202, 288; Schroeder, A. 221, 34).

**Carbon dioxide** *Carbonic anhydride, carbonic acid*  $\text{CO}_2$ ; sp.gr. (gas) 1.53 (1.5241, Regnault); sp.gr. (liquid) 1.057 at -31°; .966 at -11°; .84 at +11°; .726 at +22.2° (Cailletet and Mathias, C. R. 102, 1,202). Sp.gr. Regnault, A. Ch. [3] 26, 257. V.D. 22; 22.42 at 800°; 21.2 at 1180° (Meyer and Goldschmidt, B. 15, 1165). S.H.v. = .33 (eq. vol. air=1), .2169 (eq. wt. air=1) Regnault (C. R. 36, 676, &c.), Wiedemann (P. 157, 24). S.H.p. = 1.29 to 1.305 S.H.v.

(Amagat, Röntgen, C. R. 71, 336; 77, 1,325).

C.E. = .0037 (Regnault, Magnus, Joly).  $\frac{\text{PV}}{\text{P}_1\text{V}_1} = 1.00722$  (Regnault, C. R. 20, 975). At 200° obeys Boyle's law (Amagat, C. R. 68, 1170; 73, 183). C.E. liquid  $\text{CO}_2$  very large, 120 vols. at -20° become 150 at +30° (Thilorier, A. Ch. 60, 427). Critical temperature = 30.9° (Andrews, T. 1869, 575). Vap. pressure liquid  $\text{CO}_2$  in atmospheres (Regnault), -25° = 17.1; -5° = 30.9, 0° = 35.4, +5° = 40.5; 15° = 52.2; 25° = 66; solid (hammered) under 1.2° (Landolt, B. 17, 339). [-65° Mitchell, [-57° Faraday; [-78°] 35° = 82.2; 45° = 100.4, of solid  $\text{CO}_2$  in atmospheres (Faraday). -57° = 5.33, -70° = 2.2; -99.4° = 1.14; b.p. solid  $\text{CO}_2$ , i.e. temp. at which vap. pressure = 760 mm., is much lower than m.p. Regnault and Pouillet found -78° to -79° (P. 77, 107). (Thilorier) = -95° to -98°; (Faraday) = -99°. By evaporating solid  $\text{CO}_2$  mixed with ether a temperature of about -100° is obtained.  $\mu_{\text{CO}_2} = 1.000395$ ;  $\mu_{\text{R}} = 1.000356$ ;  $\mu_{\text{H}_2} = 1.000496$  (Croullebois, A. Ch. [4] 20, 136; also Chapman and Rivière, C. R. 103, 37). H.F.p. ( $\text{C}_2\text{O}_2$ ) = 96.96; ( $\text{CO}_2\text{O}$ ) = 67.67; H.F.v. ( $\text{C}_2\text{O}_2$ ) 96.96; ( $\text{CO}_2\text{O}$ ) 67.67; ( $\text{C}_2\text{O}_2\text{Aq}$ ) 102.84; ( $\text{CO}_2\text{O.Aq}$ ) 73.84; ( $\text{CO}_2\text{Aq}$ ) 5.88;



( $n=1=11.016$ ) ( $n=2=20.184$ ) ( $n=4=20.592$ ). Thomsen—

Solubility of  $\text{CO}_2$  gas in water:

at 0° = 1.7967	at 11° = 1.1416
1° = 1.7207	12° = 1.1018
2° = 1.6481	13° = 1.0653
3° = 1.5787	14° = 1.0321
4° = 1.5126	15° = 1.0020
5° = 1.4497	16° = 0.9753
6° = 1.3901	17° = 0.9519
7° = 1.3339	18° = 0.9318
8° = 1.2809	19° = 0.9150
9° = 1.2311	20° = 0.9014
10° = 1.1847	

absorption-coefficient

$$= 1.7967 - .07761t + .0016424t^2.$$

F F

Solubility of  $\text{CO}_2$  gas in alcohol:

at  $3\cdot2^\circ = 4\cdot0442$  at  $11\cdot2^\circ = 3\cdot2357$

$6\cdot8^\circ = 3\cdot7374$   $18^\circ = 3\cdot0391$

$10\cdot4^\circ = 3\cdot4875$   $22\cdot6^\circ = 2\cdot8277$

absorption-coefficient

$= 4\cdot32955 - \cdot09395t + \cdot00124t^2$

(Bunsen, A. 93, 1).

Carbon dioxide was known to Paracelsus and Van Helmont, and was carefully studied by Black. Its true composition was first demonstrated by Lavoisier in 1775. It was liquefied by Davy and solidified by Thilorier. It is formed by the combustion of carbon in oxygen or air. The presence of moisture is necessary for the combustion of carbon in oxygen (Brereton Baker, C. J. 1885, 349). Is a constant product of ordinary processes of combustion. It is also formed by the respiration of animals, in various processes of fermentation, and by the decay of animal and vegetable substances. It is ejected from fissures in the ground in volcanic districts, and from the craters of active volcanoes, and exists in solution in natural waters, some of which contain it in such quantities as to effervesce. It is found also in mines, quarries, wells, and caverns, particularly in limestone districts. It is a constant constituent of the atmosphere, which contains on the average about 0·034 p.c. The air in streets often contains as much as 0·05 to 0·09 p.c. In crowded rooms it may reach ·3 p.c. It is further produced by the decomposition of carbonates either by the action of heat or of stronger acids, and is frequently formed when organic bodies are subjected to high temperatures. In the reduction of many metallic oxides by carbon; by burning carbon monoxide; by heating together carbon monoxide and steam; and by the action of steam on calcium carbonate at red heat; by heating a mixture of potassium bichromate and sodium carbonate.

Best prepared by acting on chalk, marble, or magnesite with dilute hydrochloric acid solution. The gas may be collected over water or by displacement of air. On the large scale it is obtained by heating chalk or limestone to redness in iron or earthen vessels (in lime burning) or by burning charcoal. It is manufactured also as a by-product in the combustion of fuel. Also pure on large scale by heating carbonates with steam (S. C. I. 3, 568).

It is a colourless, inodorous, heavy gas, neither combustible nor a supporter of combustion. Strongly heated potassium or sodium and brightly burning magnesium burn in carbon dioxide. It liquefies under pressure of 36 atmospheres at  $0^\circ$ .

*Liquid carbon dioxide* can be obtained in large quantities by an apparatus described by Thilorier (A. 30, 122). Natterer compresses carbon dioxide by a specially constructed air-pump (J. pr. 35, 169; v. also Gore, T. 1861, 63). It is prepared from bisulphates, by the action of carbonates, the apparatus consisting essentially of a leaden vessel containing a solution of the bisulphate and having a stirring apparatus and gear fixed air-tight to it. By means of a tube and pump an equivalent quantity of calcium carbonate (obtained as a waste product in the manufacture of caustic soda) suspended in water in a second vessel is forced in and the stirrer set in motion. The liberated carbon dioxide is dried

and passed into a gasometer from which it is afterwards condensed. An apparatus is also described which allows the evaporation and expansion of liquid carbon dioxide to take place round a tube containing a solution of calcium chloride. The latter is so cooled that it may be used for the manufacture of ice. The carbon dioxide thus used is passed over moist sodium carbonate, converting it into bicarbonate which may be again used in the carbonic acid manufactory.

Liquid carbon dioxide may be bought in iron or steel bottles containing 8 kilos. (about 1,000 litres of the gas at ordinary temperature and pressure), costing about 1 mark per kilo. It furnishes the cheapest means for aerating waters, and is used for raising sunken ships, for driving torpedoes, extinguishing fires, for cooling purposes, and, as 'Pietet's fluid,' for freezing machines, and by the firm of Krupp, in Essen, for the condensation of steel and other metals, and is further suggested as a motive power for trams and balloons (C. S. I. 4, 610).

Liquid carbon dioxide is colourless, very soluble in alcohol, ether, and volatile oils, but does not mix with water. When the pressure is suddenly relieved, part of the carbon dioxide immediately vaporises, producing sufficient cold to solidify the remainder. Landolt allows the liquid to evaporate freely into woollen bags, and compresses the solid carbon dioxide in conical wooden moulds by wooden pistons (B. 17, 309).

*Solid carbon dioxide* is a white, flocculent, snow-like mass, and may be left exposed to the air for some time without sensible evaporation. An air or spirit thermometer immersed in it sinks to  $-78^\circ$ ; it can, however, be placed on the hand without any acute sensation of cold. By mixing with ether its refrigerating power is greatly increased. The cold produced in this manner is sufficient to solidify mercury, and to liquefy several gases. The cold may be further intensified by placing it under the receiver of an air-pump. (For an apparatus for collecting solid carbon dioxide, v. Dueret, C. R. 99, 235.)

Carbon dioxide when quite dry has no action upon litmus, but if moisture be present the litmus is coloured wine-red. The colour disappears on exposure to air owing to escape of the gas. Passed into lime-water, carbon dioxide renders it turbid owing to the formation of calcium carbonate, but if the gas be in excess, the neutral carbonate is converted into an acid carbonate and the liquid becomes clear.

Carbon dioxide is rapidly absorbed by a solution of caustic potash. Its solution in water has a sp. gr. 1·0018. It has a slightly acid taste, colours litmus wine-red, and partially neutralises alkalis and dissolves carbonates of barium, strontium, calcium and magnesium, &c. Its solution in water probably contains carbonic acid  $\text{H}_2\text{CO}_3$ . At ordinary temperatures, and under 1 atmosphere, the mass of carbon dioxide dissolved increases as the pressure. But at pressures of 2, 3 or more atmospheres the mass of carbon dioxide dissolved is less than that calculated by Dalton and Henry's law (v. Khanikoff and Louguine, A. Ch. [1] 11, 112).

Water which has been saturated with carbon dioxide under pressure gives it up as soon as the pressure is removed. This property is made use

of in the manufacture of effervescing drinks and aerated waters (*v. AERATED WATERS*).

Under the same pressure the volume of gas absorbed by water diminishes as the temperature rises, the whole of the gas being expelled at boiling heat. Hence carbonic acid water, holding an earthy carbonate in solution, deposits it when the water is boiled. This is the cause of the furring of kettles, boilers, &c., in which spring- or river-waters have been boiled.

Potassium burns in carbon dioxide at a red heat with a red incandescence, depositing charcoal mixed with potassium carbonate. Sodium decomposes it in a similar manner as do phosphorus and boron in presence of an alkali.

It is decomposed by the electric spark into carbon monoxide and oxygen, if hydrogen, or mercury, or some other metal is present to combine with the oxygen, otherwise the carbon monoxide and oxygen recombine to carbon dioxide. It is partly changed to carbon monoxide and oxygen by heating to 1300°C. in a porcelain tube (Dewille, C. R. 56, 729; also Berthelot, C. R. 68, 1035). Partly decomposed by electric sparks, a condition of equilibrium is attained when change of  $\text{CO}_2$  into  $\text{CO} + \text{O}$  equals that of  $\text{CO} + \text{O}$  into  $\text{CO}_2$  (Dixon and Lowe, C. J. 47, 571). Mixed with hydrogen and heated to bright redness, or submitted to induction sparks, carbon monoxide and water are formed; if the water is removed the whole is converted to carbon monoxide (Dixon, C. J. 49, 94). A mixture of carbon dioxide and hydrogen passed over red-hot pumice yields carbon and water (Dabrunfant, C. R. 74, 123).

Mixed with sulphur-vapour and passed through a red-hot tube gives carbon monoxide, sulphur dioxide, and a little carbon oxy-sulphide (Berthelot, Bl. 2] 40, 362). Passed through a red-hot tube with sulphuretted hydrogen it forms carbon monoxide, water, and sulphur (Köhler, Bl. 11, 205). Reduced to carbon monoxide by hydrogen, charcoal, iron and zinc, or copper which has occluded hydrogen (Tissandier, C. R. 74, 531, Schrotter, W. A. B. 34, 27), by potassium cyanide (Eiloart, C. N. 54, 88), by protoxides of iron and tin (Wagner, Fr. 1879, 559), and partially by ferrous sulphate, and a little water in a closed tube (Horsford, B. 6, 1390).

Carbon dioxide is reduced to carbon by heating with potassium, sodium, or magnesium. Alkaline carbonates heated strongly with phosphorus or boron give carbon dioxide, which is reduced to carbon (Tennant, Crelles; A. 1793, 1, 158; Dragendorff, J. 1861, 111; Leeds, Bl. 12, 1834 and 2131); decomposes moist potassium iodide at high temperatures, yielding hydriodic acid (Papasogli, G. 1881, 227). Solution of carbon dioxide in water yields sodium formate with metallic sodium (Kolbe and Schmidt, A. 119, 251). Carbon dioxide is assimilated by the chlorophyll corpuscles of plants under the influence of sunlight, carbon being abstracted and oxygen set free.

The specific heat of carbon dioxide is greater at high than at ordinary temperatures (Berthelot and Vieille, Bl. 41, 566). According to Hoppe-Seyler (H. 10, 201, and 10, 401), the carbonic acid and marsh-gas found in water-logged soils is due to a wide-spread process of fermentation of cellulose.

For estimating carbon dioxide in air, Ballo shakes a solution of potash and barium chloride of known strength with the air, and estimates the quantity of phenolphthalein which is decolourised by it (Ballo, B. 1884, 1097).

Carbon dioxide is used extensively in the arts for the manufacture of aerated waters, in sugar manufacture for separating lime from the juice of the sugar-cane, in bread-making, and for raising and clarifying beer. It has also been proposed to use it as a motive power where fuel is expensive (Herbert, C. C. 1885, 543, 558, 572). It also possesses antiseptic properties and retards the putrefaction of meat (Kolbe, J. pr. 2] 28, 61).

**Carbon disulphide** *Thiocarbonic anhydride*, *sulphocarbonic acid*  $\text{CS}_2$ . This compound was accidentally discovered by Lampadius, in 1796, by heating pyrites with charcoal. Clement and Desormes, in 1802, examined the action of sulphur on red-hot charcoal, when they obtained a product similar to that of Lampadius. The nature of the liquid was established by Vauquelin.

**Manufacture.**—Schrotter, in Germany, and Peroncel, in France, first prepared carbon disulphide on a manufacturing scale. Schrotter employed a cylinder of Hessian clay in which the charcoal was heated; the sulphur was introduced through a hole near the bottom of the cylinder, and there was fixed to the upper end of the apparatus an exit tube for the vapour of the carbon disulphide formed. This apparatus would produce about 20 kilos of the disulphide in 12 hours, and it represents the type of the processes since employed in the production of this substance on the manufacturing scale.

Deiss and Fisher employed cast-iron cylinders in which the vapour of sulphur passed over charcoal was heated to redness. Fireclay retorts were next introduced, glazed internally to prevent the escape of vapour through the pores; each cylinder was about 5 feet high and nearly 20 inches diameter. Four retorts were arranged in a single furnace in such a way that the flame of the fire could play entirely round them. Each retort was divided internally into two parts by means of a perforated shelf; the upper compartment, which was the larger of the two, served to contain the charcoal, which could be thrown in through a special opening in the lid without interrupting the working. A second opening in the top of the retort was provided with a tube about two inches in diameter, which led directly into the lower compartment, and was used to throw in sulphur as required. The vapour of carbon disulphide which was formed during the process was conducted through a delivery pipe connected with a third opening in the retort into the condensers. The four retorts having been filled with charcoal and the lids closed, were heated to redness by a coal fire. Pieces of sulphur wrapped in cylindrical paper packets were then dropped in the pipes leading to the lower partitions of the retorts. Two such packets, each containing about  $5\frac{1}{2}$  ounces of sulphur, were thrown in at intervals of about three minutes, the opening at the end of each tube being closed at each successive addition. The charcoal was renewed every seven hours, and was heated about an hour and three-quarters each time before the necessary



temperature was attained for its combination with sulphur. The vapour of carbon disulphide mixed with that of sulphur escaped through the delivery tubes, passing into the first row of condensers, where it was partially condensed, together with some sulphur, the undissolved sulphur depositing in the solid state, and could be recovered and used over again. From thence the uncondensed vapours passed on into the second row of condensers, and so on till the last row. The condensers, amounting to 18 or 20 in all, were connected together by pipes, the last of which was connected with the chimney of the works, or better, with vessels or tubes containing layers of pulverised lime to absorb the sulphuretted hydrogen which would otherwise create a nuisance in the neighbourhood of the works.

The condensers were made of sheet zinc, were cylindrical in shape and about 26 inches in diameter, bottomless, with slotted sides, and stood in a kind of shallow cistern containing water a little deeper than the openings, so as to form a water-lute, permitting the passage of condensed liquids while closing the exit against vapours. The lids of these condensers were furnished with rims forming a kind of saucer containing water to assist in the condensation of the vapours. Each lid had two openings in the form of tubulures, into which the pipes were fixed for the transmission of the vapours from condenser to condenser.

Gérard employed a vessel of cast iron 6½ feet in height, about 4 feet 8 inches in diameter, and

disulphide passed forward into the condensers. The condenser consisted of three vessels, cylindrical in form, arranged vertically one above the other, and communicating by vertical pipes. The topmost condenser had an exit pipe for sulphuretted hydrogen, &c., and the condensed carbon disulphide could be drawn off into a receiving vessel beneath by opening a cock in a pipe proceeding from the lower condenser.

The three condensers were contained in a tank 5 feet high and 5 feet wide, filled with water, which could be renewed at pleasure.

The addition of sulphur was continued for ten hours daily in portions of about 3 lbs. at a time of three minutes' interval. The oven was heated during the night to volatilise the sulphur, and the residue of charcoal was used up by mixing with the new charge. This apparatus yielded in twenty-four hours about 570 lbs. of carbon disulphide, which in theory requires 480 lbs. of sulphur and 90 lbs. of carbon for its production, but in practice 530 lbs. of sulphur and 242 lbs. of wood-charcoal were used. Gérard found it advantageous to surround the generating vessels with brickwork, which renders them much more durable, and capable of lasting about two months.

It was found in practice that retorts could not be employed with economy beyond a certain size, as when they were too large the heating was irregular, causing considerable waste of sulphur. When using unrefined sulphur the retorts needed cleaning every fortnight, but with purified sulphur they could be kept working for two months.

The following account of the present mode of manufacture is due to Ignatius Singer (S. C. I. 8, 1889, 93:—

A is a vertical cast-iron retort, or, better still, made of earthenware, glazed inside, of elliptical shape, about 66 inches high, and 20 by 12 inches internal diameter. It rests on a support, *v*, made of fire-bricks, and is protected by a mantle of best fire-bricks, *c*, about 4 inches thick, leaving a space of from ½ to ¾ inch between it and the retort. The metal of the retort should not be less than 2 inches in thickness. *b* is the outer brickwork of the furnace lined on the inside with fire-bricks, *b'*; *rr*, fire-grates; *e'*, ash pits; *r*, furnace doors, made of frames, *a*, into which a fire-proof slab, *b*, is inserted. The furnace doors are suspended by cables running over pulleys, and are counterpoised, so that they can be raised or lowered. At *d* is shown a small peep-hole, through which the temperature in the furnace may be watched. In the lid of the retort are cast two tubes, *g* and *g'*, of about 5 inches internal diameter and not less than 1 inch in thickness, but it is advisable to have them made somewhat stronger, as the lid will then outlast several retorts. Over the openings, *g*, a vent-pipe or flue, *h*, is suspended by a lever, so that it can be raised or lowered at will, one end of which passes through the roof. When fresh charges of charcoal are to be introduced into the generator *A*, which is done through the tubulure *g'*, the lid closing the tube *g* is first removed, and the vent-pipe *h* quickly lowered, which serves the purpose of carrying off the noxious gases that would otherwise be injurious to the workmen. *g'* may now be opened, and

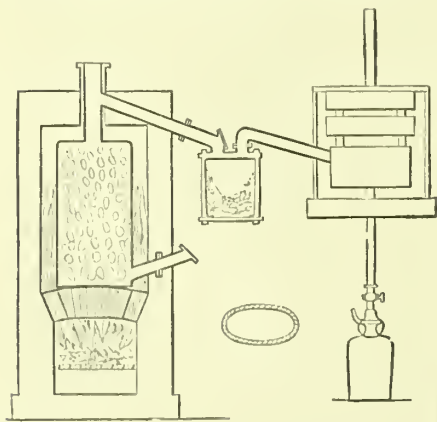


FIG. 1.

sides 1½ inch thick. The retort was elliptical in section, stood upon a brickwork arch, and was heated from below by a fire. Near the bottom was a pipe fitted with a valve, through which sulphur could be introduced into the cylinder. At the upper extremity there was a wide pipe which could be closed with a lid, and served for the introduction of charcoal into the apparatus. Another pipe, cast in one piece with the upper one, sloped forward and passed into a receiver in which the sulphur which passed over during the operation was condensed, and could be easily removed by opening a valve in a tubulure placed at a bend in the pipe; the more volatile sulphur

the carbon fed in without the slightest inconvenience.

From the tubulure *a'* issues a pipe, *r*, inclined upwards, through which the bisulphide of carbon vapours escape. Most of the free sulphur passing over will condense here and run back into the retort. But the partially cooled sulphur falling on to the surface of the incandescent carbon would be immediately vapourised again, at the same time cooling down the top layer of the charcoal. To obviate this Singer suggests that an opening should be made in the lower part of the pipe *r*, to which a hopper can be fitted, as shown at *j*, terminating in an earthenware pipe *k*, reaching nearly to the bottom of the retort. By this means the sulphur distilling over uncombined would be conducted back to the bottom of the generator, the pipes would be

less liable to be choked up, while the resulting product would be purer.

From the lower end of the retort, close to the bottom, a pipe *m* branches off, a little upwards inclined, passing through the brick-work and terminating in a chamber *x*, with door *n*. During work this pipe is carefully closed by a lid. It serves the purpose of raking the ashes out of the retort, which is done once a week. At *m* a flue is shown, carrying the noxious gases into the chimney. The ashes are allowed to cool here before their removal. Adjoining this chamber is a hearth into which an iron vessel *o* is fitted, for melting the sulphur. It is heated by a flue from the furnace passing underneath it, provided with a damper to regulate the heat. (In fig. 2 this sulphur vessel is raised so as to make it visible in the

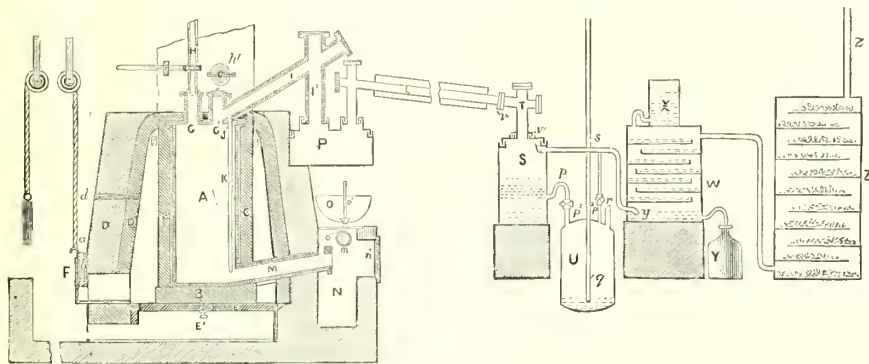


FIG. 2.

drawing.) A pipe *o*, closed by a conical valve to which an iron rod *o'* is attached, connects the sulphur-pot with the arm *m* of the retort, by which means the sulphur can conveniently be introduced into the latter.

The sulphur flowing down the incline of the arm *m* arrives at the bottom of the retort, where it is volatilised; the vapours, passing upwards, combine with the carbon. The generated bisulphide vapours escape through pipe *r*, and then pass down the vertical tube *r'* into a vessel *p*, where any excess of sulphur is deposited. The lid of this vessel rests in hydraulic seals, and is connected with the inlet and outlet pipes by a kind of telescopic tube made air-tight by water. When the vessel *p* is to be removed, the lid is raised, the vessel taken away, another similar one put in its place, and the lid lowered again. This should be done once a week only, and never while distillation is going on.

The carbon bisulphide vapours, now freed from the greater part of uncombined sulphur, pass through a Liebig's condenser, *l*, about thirty feet long, into a receiver, *s*, partially filled with water. The crosspiece *r*, connecting the Liebig's condenser with the receiver, is made so that it can be detached—being secured at *v* by flanges bolted together, and at *v'* by water seal—for purposes of cleaning, &c. From here the bisulphide is allowed to run through a syphon *p*, direct to the storage tanks. A better plan, however, is to keep the storage tanks for the crude product on a high level, which greatly

facilitates the after-process of purification. In this case the bisulphide of carbon is allowed to flow into a *montejus*, *u*, as shown in drawing. A pipe *q*, reaching nearly to the bottom, is passed through the cover of the *montejus* to the high-level tank. A second pipe, *r*, connects the vessel *u* with a force-pump. On air being pumped into *u* through *r*, the stop-cocks *p'* and *p''* having been shut off, the bisulphide is pressed up through pipe *q* into the tank. This is a far better method than using pumps, as in the latter it is difficult to prevent leakage, the crude bisulphide having a very corrosive action on most metals. For the same reason, the receivers, tanks, &c., for the crude substance should all be lined with sheet-lead, as wrought-iron vessels soon perish, while copper is even more energetically acted upon. Cast iron withstands corrosion much better, but is objectionable on account of its porosity. This might be remedied, however, by giving the vessels repeated coatings of dilute silicate of soda, both inside and outside, the vessels being first slightly heated with steam and the silicate applied while warm.

Near to the top of the receiver *s* is a pipe, *s*, for carrying off the uncondensable vapours—chiefly sulphuretted hydrogen. The gases are conducted into a rectangular vessel, *w*, where they are made to circulate in zigzag over a series of shallow trays filled with a vegetable oil, to absorb any bisulphide vapours which have escaped condensation. The oil can be made to trickle from a reservoir, *x*, as shown, through a goose-

necked pipe, which, passing from tray to tray in an opposite course to that of the gases, finally trickles through *x* into a receiver, *y*. When a sufficient quantity has accumulated here, the bisulphide is distilled off and the oil returned to *x*. Before the gases enter this absorber they are 'washed' by making the end of the pipe *s* dip into the oil as shown at *y*, whereby the apparatus is disconnected from contact with air. The gases are now passed through a second vessel, *z*, similar in construction to the one just described, only substituting lime or oxide of iron for the oil, to absorb the  $H_2S$ , and are then allowed to escape into the open air through the pipe *z*.

Above the retort *a*, and between it and the chimney, set at right angles to each other, is a smaller retort, similar in construction to *a*, but only about one-third the capacity of the latter, and is heated by causing the products of combustion coming from the furnace to circulate round it before finally passing into the chimney. (Only the discharge hole *h'*, corresponding to the arm *m* of the retort *a*, is visible in drawing.) As the generator *a* requires fresh charges of carbon every eight hours, it is very economical to keep this small retort always filled with charcoal, which by the time it is required will be red hot, and no more time need be lost than is required for transferring it from the one into the other retort. By this arrangement, part of what would otherwise be waste heat is utilised, and a great saving in time and fuel effected. A still better plan is to make the charcoal on the spot, eight hours being more than sufficient to char the wood and to heat it up to bright redness. The spent dyewoods, tanners' refuse, or sawdust, are excellent for the purpose, and as these would not require crushing—as when charcoal is bought in lumps—a saving in labour, possibly also in money, might be made, besides being more cleanly. By a small outlay the vapours might be condensed, and pyroligneous acid obtained as a by-product.

The apparatus is worked as follows. After having allowed the brickwork to set and partially dry for a few days, the fires are started, at first gently, to prevent the brickwork from cracking, then gradually increasing the heat until the retort becomes a dull red colour. The latter is now filled with small charcoal, and the smaller retort with chips, sawdust, &c., and the fires are now urged until the retort and the charcoal in it have become a 'cherry red.' This heat should never be exceeded, nor should it be allowed to fall below this, as in either case it would result in a lesser yield of carbon disulphide.

When the proper temperature is attained, the two openings in the lid of the retort are closed, the lids being screwed down tightly, with some clay made into a thick paste as a lute. A better way would be to cast in the top of these tubular grooves, and the lids with a rim loosely fitting into these grooves, forming what is called an hydraulic seal, only using lead in the place of water. The heat there is sufficient to melt lead, but not so great as to prevent its use. This would form a much better lute, and could be opened and closed in much less time, which, in the case of bisulphide of carbon manufacture, is a great desideratum. Having previously secured all the joints throughout the apparatus, sulphur

is now run in by raising the rod *o'* in the sulphur pot. A bubbling will immediately be heard in the gas-washer at *y*, caused by the escape of sulphuretted hydrogen &c. In a few minutes this bubbling ceases, and carbon bisulphide begins to distil over. Distillation is now proceeding, sulphur being charged in every five minutes, about  $1\frac{1}{2}$  to 1  $\frac{1}{4}$  lbs. each time, for seven hours, when the supply of sulphur is stopped, and one hour allowed to elapse before fresh charcoal is filled in. The lid is then removed from *c*, and the flue-pipe *n* lowered. *c'* may now be opened, and last of all the lid *h'* is removed from *h* of the carboniser, and the red-hot charcoal raked from the carboniser, by means of a funnel or hopper, into the retort *a*. The retort is now closed, taking care that the opening communicating with the flue *n* is the last to be shut off, and work started again. At the end of each week neither coal nor sulphur is charged

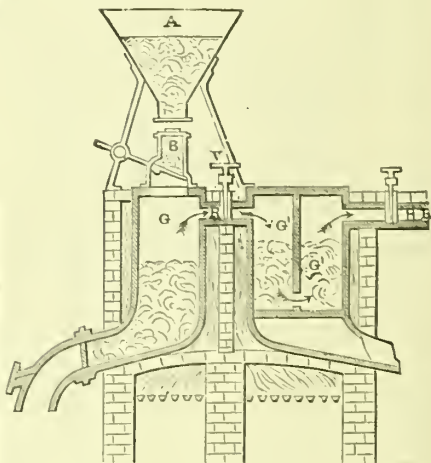


FIG. 3.

in for eight hours, after which the whole apparatus is cleaned out in the following manner. The flue *n* having been lowered on to *G* as described above, the cover at the end of the delivery pipe *r* is removed, and wet bags or pieces of canvas are tightly rammed down the pipe *r*, and past its junction with the vertical pipe *r'*, so as to isolate the condensers &c. from the furnace. The ashes are now raked out through *m*, as described above, the retort refilled with fresh charcoal, and while this is getting heated up, the other portions of the apparatus are examined, and where sulphur is present it is removed.

With one such retort, from 4 to 5 cwt. of carbon bisulphide can be made in a day, but it is much more economical, both in labour and fuel, to have several retorts—say four—in the same furnace.

Pyrites may be used instead of sulphur in the manufacture of carbon disulphide, and figure 3 shows an arrangement for this purpose devised by Labois. The pyrites is fed from the hopper *a* into the distributing box *b*, whence it passes into the roasting compartment *c* by the valve which is worked by a lever. The sulphur vapour is conducted through



an opening at *a* which can be regulated by the valve *v*; it has then to traverse the heated coke in *g'* as indicated by the arrows, the vapour of carbon disulphide formed passing out at *a'*, and thence to the condensing apparatus (Sc. Am. Supt. 12, 4763).

As the latent heat of carbon disulphide vapour is much less than that of steam, it follows that the former need be deprived of only a small amount of heat to insure its condensation; it is, therefore, on this account advisable to surround vessels from which it is distilled with bad conductors of heat, otherwise a large amount of the vapour condenses before reaching the condensers, and flows back into the distilling vessel.

In the manufacture of carbon disulphide the yield depends mainly upon the temperature employed. Sidot has shown that by passing a known weight (40 grams) of sulphur vapour over 10 grams of charcoal contained in a porcelain tube heated to various temperatures, varying amounts of the disulphide are obtained, and he gives the following numbers, representing the mean results of three experiments at each of the temperatures indicated.

1. At a dull red heat, 5 grams of carbon gave 17 grams disulphide.

2. At a red heat 6.3 grams of carbon gave 29 grams disulphide.

3. At a bright red heat 7.5 grams of carbon gave 19 grams disulphide.

These numbers show clearly that to obtain the maximum yield a red heat should be employed.

*Purification of carbon disulphide.*—The crude product, which contains considerable quantities of sulphur, may be purified by distillation. The distilling vessel is made of sheet zinc, and is fitted in a water-bath. The vapours of carbon disulphide are passed through a wide tube into a worm surrounded by cold water, and ending in a lap at the bottom; the liquid as it condenses is allowed to trickle into a vessel placed to receive it.

Deiss employed large boilers with flat bottoms, which were 10 feet in length,  $6\frac{1}{2}$  feet in diameter, and  $3\frac{1}{2}$  feet high. They had domed covers, externally coated by badly conducting material, so as to reduce to a minimum the amount of carbon disulphide returned to the boiler by condensation. The boiler was capable of receiving 5 tons of crude disulphide at a single charge, and had six delivery tubes which terminate in six vertically placed condensers. At the bottom of the boiler there are two serpentine pipes, through one of which steam is passed until the crude carbon disulphide boils. For the purpose of distilling off the last portions steam is passed through the second serpentine pipe direct into the boiler, by which means carbon disulphide vapour and steam pass over together into the condensers, when the former accumulates in a layer below the surface of the water. The distillation of 5 tons lasts three or four days, and the products of the distillation at different stages are separately collected, and serve for different purposes. In the first portions foul-smelling constituents predominate, such as sulphuretted hydrogen; the intermediate portions are the purest, while the last

portions are contaminated with sulphur. Much of the sulphuretted hydrogen may be removed by placing a small quantity of caustic soda in the boiler.

Bonière purified the crude material by running it into a still containing a strong solution of caustic soda and heated externally by steam; the vapour was then passed through several other vessels of a similar kind containing alkaline liquids, solutions of salts of iron, lead, or copper, from which it is distilled and condensed. Millon patented a process which consists in mixing the disulphide with half its weight of milk of lime, and then carefully distilling.

Sidot first distils the crude product, and then agitates it with mercury till the shining surface of the metal is no longer blackened by it. Carbon disulphide when pure is not affected by contact with mercury for any length of time. Or it may be shaken with 0.5 p.c. of mercuric chloride, which removes a fetid compound of sulphur. The clear liquid is then decanted, 0.02 of its weight of an inodorous fat is added, and the mixture distilled in a water-bath at a low temperature (Cloez).

Another method of purification is to add to 100 parts of commercial product from 2 to 3 parts of dried copper sulphate, and shake the mixture. The copper salt blackens and settles down, with removal of the smell of sulphuretted hydrogen. Absolute purity is obtained by again rectifying over dry copper sulphate. The latter can be rendered fit for further use by ignition, treating with sulphuric acid, and again igniting. The sulphide may be retained in a state of purity by allowing it to stand constantly over dry copper sulphate (S. C. I. 2, 246).

Singer has employed the following simple method with very satisfactory results:

A cylindrical vessel, about 30 inches in diameter and 6 feet high, is provided with a perforated coil of lead pipe at the bottom. Into this vessel the impure carbon disulphide is run to about one-third its height. Lime-water is then pumped into it by means of a force-pump through the perforated coil. The lime-water being specifically lighter than the carbon disulphide rises to the surface, and while traversing the body of the disulphide in a finely divided spray, the lime combines with the sulphuretted hydrogen, &c. This washing is continued until the lime-water, which leaves this vessel through an overflow pipe near to the top, is perfectly clear. The carbon disulphide is now run into a still, about 1 p.c. its weight of a cheap colourless oil added, and covered with a layer of about one inch of water, to which some sugar of lead may be added. The carbonate disulphide is now distilled in a water-bath and condensed in the usual way.

Carbon disulphide comes into the market in sheet-iron drums, the plates forming the top and bottom being bent inwards for their better protection from blows in moving about, and in the upper end there is an opening which can be closed by a screw stopper. Great care should be taken in the storing of carbon disulphide on account of its extreme volatility, the explosive nature of a mixture of the vapour with air, and the fact that its products of combustion are three irrespirable gases, viz. carbon dioxide,

sulphurous oxide, and nitrogen. The store room ought to be isolated from other buildings, and should be well ventilated. The vessels in which the substance is kept ought to be tolerably large and placed where they are not likely to receive a blow or get thrown over. When required for use the carbon disulphide can be drawn off by means of a siphon.

*Properties.*—Carbon disulphide is a colourless, heavy, and extremely volatile liquid; the commercial product has a repugnant and fetid smell, but when purified it has a sweetish ethereal odour, and an acrid pungent taste. It is highly refractive, its power in this respect being 1.645; its sp.gr. is 1.29215 $\frac{9}{4}$  (Thorpe). Water dissolves about  $\frac{1}{1000}$  of its volume of the disulphide, and yields it up again unchanged on distilling; the solution in water possesses the odour of the disulphide, and has a slight burning taste. The aqueous solution acts as an antiseptic. Carbon disulphide dissolves sulphur, phosphorus, iodine, bromine, chloroform, camphor, caoutchouc, oils, and fats, and may be mixed in almost any proportions with alcohol, ether, benzene, and the fixed and volatile oils. Sulphur and phosphorus may be obtained in crystals by the spontaneous evaporation of their solutions in carbon disulphide. When a rapid stream of air is passed through it, the vapour, as it rises, is condensed to cauliflower-like masses, which make their appearance on the surface of the liquid (Wartha, B. 3, 80). When the whole of the liquid has disappeared, the resulting solid has a constant temperature of  $-12^{\circ}$ , so long as it remains unvolatilised. According to Wroblewski and Olzewski it solidifies at  $-116^{\circ}$ , and remains solid for a considerable time, emitting a peculiar aromatic odour.

Carbon disulphide boils at  $46.6^{\circ}\text{C}$ . (Thorpe), and the vapour ignites in air at  $149^{\circ}\text{C}$ . When mixed with three times its volume of oxygen, or an amount of air containing that volume of oxygen, it is very explosive. The flame of burning disulphide of carbon is blue, and gives rise to sulphurous and carbonic acid gases:  $\text{CS}_2 + 3\text{O}_2 = \text{CO}_2 + 2\text{SO}_2$ . When carbon disulphide is burnt in a lamp on the principle of the Bunsen burner, and special precautions taken to prevent explosions, it produces a flame with an actinic power superior to that of magnesium (C. R. 79, 1078).

A mixture of the vapour of disulphide of carbon with nitric oxide burns with a blue flame, which is very rich in rays of high refrangibility, and on this account has been employed in photography.

Carbon disulphide is highly poisonous, inhalation of the vapour producing giddiness, vomiting, congestion, and finally coma. When taken in small quantity only, it produces in time very serious effects on the nervous system. In the workmen employed in its manufacture it causes weakness, depression, and loss of memory. Solution of ferrous carbonate in carbonic acid water has been found in some cases effectual as a remedy. Carbon disulphide vapour, when passed through a tube heated to bright redness, is partly resolved into its elements, carbon depositing and sulphur passing off with the undecomposed compound. When a long thin plate of gold or platinum wound into a spiral with tin-foil is immersed in carbon disulphide, the latter is said

to be decomposed, sulphur combining with the tin, and carbon being deposited in small crystals (C. R. 63, 213).

The following table represents its tension at varying temperatures (Seyferth):

45.5°C.	. . . . .	1 atmosphere
57.7 . . . . .	. . . . .	1 $\frac{1}{2}$ "
66.9 . . . . .	. . . . .	2 atmospheres
74.3 . . . . .	. . . . .	2 $\frac{1}{2}$ "
80.6 . . . . .	. . . . .	3 "
86.1 . . . . .	. . . . .	3 $\frac{1}{2}$ "
90.9 . . . . .	. . . . .	4 "
95.5 . . . . .	. . . . .	4 $\frac{1}{2}$ "
99.0 . . . . .	. . . . .	5 "

For table of vapour pressures between  $0^{\circ}$  and  $50^{\circ}$  v. Ramsay and Young, C. J. 47, 653; also Herwig, P. 137, 69; 141, 83; 147, 161.

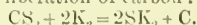
The vapour of carbon disulphide when passed over metallic oxides at a red heat yields the dioxide of sulphur and carbon, together with metallic sulphides, which are generally found crystallised and resemble those found in nature. Carbon disulphide is one of the most powerful sulphurising agents known, and by means of it many sulphides may be produced which are not otherwise obtainable (Fremy). It converts oxides into sulphides when heated with them in sealed tubes. The vapour is strongly attacked by nitric acid, yielding sulphuric acid and nitrous vapours.

A mixture of the vapour of carbon disulphide and sulphuretted hydrogen gas when passed over red-hot copper yields copper sulphide and marsh-gas:  $\text{CS}_2 + 2\text{SH}_2 + \text{Cu} = 4\text{CuS} + \text{CH}_4$ .

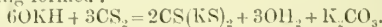
The vapour of carbon disulphide when passed over wood undergoing destructive distillation alters the character of the carbonaceous residue, producing a material having high conducting powers for heat and electricity, and extremely sonorous when struck.

Carbon disulphide is a powerful disinfectant. Meat and other putrescible bodies have been kept in an atmosphere containing the vapour of this compound for months without change.

Heated potassium burns in the vapour of carbon disulphide with formation of potassium sulphide and liberation of carbon:

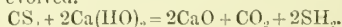


When brought in contact with a solution of an alkaline hydrate, carbon disulphide is decomposed, a carbonate and a sulpho-carbonate being formed:



In contact with solutions of alkaline sulphides, carbon disulphide also forms sulpho-carbonates;  $\text{SK}_2 + \text{CS}_2 = \text{CS(KS)}_2$ .

When the vapour of carbon disulphide is passed over heated calcic hydrate, it is decomposed, carbon dioxide and sulphuretted hydrogen being evolved.



This reaction has been utilised in the removal of carbon disulphide from coal gas, which is the chief source of the smell in illuminating gas.

Chlorine has but little action on carbon disulphide at the ordinary temperatures, but in the presence of iodine, the chlorides of antimony, and molybdenum, &c., chlorine quickly replaces the sulphur with conversion of the carbon disulphide into carbon tetrachloride, and if the action is interrupted before it is complete, intermediate

compounds or sulphochlorides are formed (S. C. I. 6, 728).

Carbon disulphide combines with triethyl-phosphine  $P(C_2H_5)_3$  to form a solid compound, crystallising in red crystals of the composition  $P(C_2H_5)_3CS_2$ .

Carbon disulphide is not decomposed by boiling water under the ordinary pressure of the atmosphere. Owing to its volatility it may be made to produce great cold by its own evaporation, and if this takes place very quickly under the air-pump a cold of  $-60^\circ C.$  may be obtained.

An aqueous or alcoholic solution of caustic potash boiled with carbon disulphide yields with lead salts a black precipitate of lead sulphide. This is a delicate test for the substance.

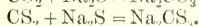
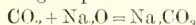
Carbon disulphide may be detected in coal-gas by passing the gas when completely freed from sulphuretted hydrogen over red-hot copper foil, when the copper acquires an iridescent lustre, and its nitric acid solution diluted with water yields after some time a precipitate with barium chloride (A. Vogel, Fr. [2] 6, 253).

Carbon disulphide may be regarded as the analogue of carbon dioxide :

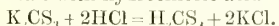
$CO_2$  carbon dioxide

$CS_2$  carbon disulphide.

It is also analogous to carbon dioxide in its chemical combinations, *e.g.* while carbon dioxide combines with metallic oxides forming carbonates, carbon disulphide combines with metallic sulphides forming sulphocarbonates :



Sodium carbonate and sulphocarbonate possess a similar constitution, and by the action of strong acids they should give analogous products, the one carbonic acid, and the other sulphocarbonic acid. Sulphocarbonic acid is a yellow oily liquid, obtained by decomposing its potassium salt with hydrochloric acid



Potassium sulphocarbonate is used for the destruction of phylloxera.

*Uses.*—The low price at which carbon disulphide can be produced has rendered its application possible to a large number of useful purposes, the chief of which is in the preparation of vulcanised caoutchouc, and as a solvent for the latter in the manufacture of waterproof goods, by the deposition of a thin layer of the dissolved caoutchouc on the fabric. It is extensively used for the extraction of fat from crude wool, for the extraction of fatty oils from oil seeds and pressed residues, and for the purification of paraffin. It is used in the extraction of uncombined sulphur, and of bitumen from minerals. It is employed by the shoemaker in making seamless joints; for the preparation of caoutchouc cement; in the manufacture of aluminium, various colours, ammonium sulphocyanide, &c. It is also used for filling prisms on account of its high dispersive power. Attempts have been made to use it in boilers instead of water, as it is converted into vapour with a much less expenditure of heat than water.

Advantage has been taken of its poisonous properties to expel weevils from grain without injuring the cereal. For this purpose a small

quantity of the carbon disulphide is inclosed in an air-tight chamber with the grain; in a few hours both the larvæ and eggs are killed without injury to the grain (Doyère). It is also used in Brazil to expel the Sauba ant from the foundations of houses. It may also be used in the analysis of oil seeds as a solvent for the purpose of ascertaining the proportion of oil which the ground seeds contain.

As carbon disulphide dissolves iodine in large quantity, but does not appreciably dissolve in water, it is employed for determining the amount of moisture in commercial iodine.

It is used as a substitute for ether in dissolving quinine and other alkaloids, for extracting the aromatic principles from seeds and spices, and for the extraction of the scent of flowers. For these purposes, however, the purest quality of the disulphide can alone be employed.

A solution of phosphorus in carbon disulphide has been employed in the electrotyping of very delicate objects, such as grasses, flowers, feathers, &c. Any of these are dipped into the solution, then, by a short exposure to the air, the carbon disulphide evaporates and leaves a thin film of phosphorus on the surfaces; they are then dipped into a solution of nitrate of silver, by which silver is precipitated in a very minute film, upon which, by the electrotype process, any thickness of silver, gold, copper, &c., can be deposited. If a few drops of carbon disulphide are put into a solution of cyanide of silver, from which the metal is being deposited upon the article to be electrotyped, the silver is deposited bright, whereas without the disulphide it would be dull.

Deiss, who first employed carbon disulphide in the extraction of fatty oils from seeds, oilcakes, and other pressed residues, used the following arrangement.

Carbon disulphide was introduced into a large cemented brickwork reservoir, with a man-hole, which is generally kept closed, 22 feet long, 6 feet in diameter, and nearly 6 feet deep, and lined with lead up to the point to which it was filled with the disulphide and water, the latter being added as a thin layer to prevent the too rapid evaporation of the carbon disulphide. Immediately above this reservoir is a worm condenser, whose tail pipe dips into the liquid in the reservoir below; on one side of the condenser there is an extractor having a capacity of 4,400 gallons, and capable of receiving a charge of 12 tons of oilcake. This extractor is supplied by means of a pump with carbon disulphide from the reservoir below through a pipe leading up from the reservoir to the extractor. The latter apparatus has two perforated shelves, one nearly at the top and the other nearly at the bottom, between which the substance to be operated upon is placed. In the space between the lower perforated shelf and the bottom of the extractor is a coil of pipe through which steam can be passed. Just above the upper perforated shelf there are nine pipes on the same level for the purpose of carrying the vapours produced in the operation to the condenser. There are also pipes just above this shelf which are in direct communication with a still on the opposite side of the condenser, to which disulphide saturated with oil is carried, the saturated disulphide



rising to the surface in the operation owing to the difference in the sp.gr. of the carbon disulphide (1.29) and oil (about 0.900). The still in which this liquid is distilled is about 11 feet long, 5 feet wide, and 15 inches deep, holding when half filled about 400 gallons. The liquid is heated by steam supplied through two pipes coiled several times round the bottom of the still, and the vapour of the volatilised carbon disulphide is led through nine pipes into the condenser, and thence into the reservoir below the condenser, and is ready to be used again in the extractor for macerating a fresh quantity of material.

The last traces of carbon disulphide are removed from fat or oil in the distilling apparatus by passing steam directly into the apparatus until all the carbon disulphide is volatilised and carried away by the steam.

The termination of the extraction in the macerating vessel is determined by the colour of the liquid, which can be seen through glass tubes fixed in the pipes conducting the liquid from the extractor to still. As soon as this is colourless the operation is considered complete, and the contents of the extractor are then discharged by opening a cock in a pipe leading to the reservoir.

When this operation is over, superheated steam is passed into the extractor in order to remove the last traces of carbon disulphide, and when the exhausted material has thus been sufficiently cleaned, a cock at the bottom of the extractor is opened and the condensed water let out; the lid and upper perforated shelf are then removed, and the residues spread out in the air to dry. These residues are used in Pisa for heating the boiler, which thus supplies steam for the whole apparatus.

The time taken to fill the extractor with carbon disulphide is eight hours, the maceration of the material four hours, the emptying of the contents of the extractor into the reservoir at the close of the operation two hours, and the steaming of the oil in the still in order to free it from carbon disulphide from eight to twelve hours. Working with an apparatus such as described, about  $2\frac{1}{2}$  tons of oil can be obtained in thirty hours from 25 tons of oilcake.

*Extraction of fat from wool.*—Morson and Jerome employ for this purpose a large cylindrical vessel with a close-fitting cover and double walls, between which hot water circulates. The wool is placed on a perforated shelf near the bottom of the cylinder, while a perforated plate, a kind of piston, could be pressed upon the wool by an arrangement of screws. Carbon disulphide is pumped from a reservoir into the extractor, and the disulphide as it becomes saturated with fat is led through a pipe into a still which is heated by a coil of steam pipe at the bottom, the vapour being passed to a worm condenser and the liquid disulphide passed into the reservoir which is immediately beneath. By a second arrangement of steam pipes, steam can be passed directly into the still so as to remove the last portions of disulphide. A current of air heated to 70° is then forced through the wool by means of an air-pump. As all the parts of the apparatus are in direct communication with each other, it is necessary to supply

the diminished pressure in the reservoir. When air is pumped out of it and sent through a tube several times bent and the last portion fitted with a hot-water jacket, the equilibrium of pressure should be maintained, and this is done by a supply of air from a gas-holder in connection with the apparatus. The last portions of carbon disulphide are thus swept out of the extractor and are carried through a pipe into a second worm condenser, and thence to the reservoir. At convenient points between the macerating vessel and the still, as well as at the ends of the condensing worms, there are windows in the pipes, which serve to form an idea of the state of the operation, and close to each of these windows is a cock from which a little of the liquid can be drawn and evaporated, in order to see if a residue of fat remains.

The macerating vessel or extractor is charged with about 10 tons of wool, and is then reduced to about half its volume by screwing down the perforated plate. The carbon disulphide is then pumped into the extractor, and after filtering through the wool ascends through the perforations and passes into a pipe leading to the condenser. This is continued until the liquid comes over colourless, and leaves no residue on evaporation. When the extracting process is finished the cock admitting carbon disulphide into the extractor is closed, and a partial vacuum is formed by drawing air out of the extractor by the air-pump, the greater part of the disulphide adhering to the wool being carried with it at the first few strokes. When this is done the water jacket is heated by water at 70°C. and the cocks are so arranged as to allow the heated air to pass through the wool, and thence into the open air. By this method a considerable quantity of fatty substance is obtained from sheep's wool which was formerly lost.

The following materials are treated with carbon disulphide in order to obtain the fatty ingredients which they contain:—

1. The dark-coloured tar-like residues of stearin manufactories, which are products of the treatment with sulphuric acid. They yield from 18 to 20 p.c. of fatty acid, which was formerly almost entirely lost. The residues are mixed with sawdust to facilitate the filtration of the dissolved portion.

2. The dark-brown cart-grease from the axles of carts, carriages, &c. This is first treated with sulphuric acid, washed, and dried.

3. Tow and rags used in cleaning machinery. This treatment of rags &c. has a threefold advantage; recovery of fat or fatty acids, purification of the rags so that they can be used again, and the prevention of spontaneous combustion which these materials are liable to on exposure to air.

4. The refuse of the preparation of beeswax, which on treatment with carbon disulphide yields a yellow wax useful for many purposes.

5. Sawdust that has been used for filtering oils after purification with sulphuric acid.

6. The dirty sediment produced by the treatment of various oils with sulphuric acid contains about 50 p.c. of oil, which may be extracted by carbon disulphide after washing with boiling water, drying, and mixing it with sawdust.

7. Bones from slaughter-houses and kitchens that are to be used in the preparation of bone-black yield with carbon disulphide from 10 to 12 p.c. of fat.

8. The expressed residues of oil seeds, such as rape, sesame, flax, &c., when they cannot be properly employed as fodder. In all cases it is necessary to break up the oilcake into small pieces before treating it with carbon disulphide, so as to ensure thorough penetration of this substance. The residue left after extracting the fat is hardly suitable for fodder, but is valuable as a manure.

9. The 'cracklings' or greaves obtained by the melting of tallow.

10. The pressed cacao-beans from which no further cacao butter can be obtained by pressing.

11. The pressed residues obtained in the preparation of olive oil.

*Extraction of bitumen &c. from minerals.*—

This process, employed by M. Moussu, is interesting from the fact that it can be employed for the extraction of bitumen from mineral bodies which contain so small a percentage as not to pay when obtained by the ordinary process of distillation. It consists of a close reservoir for the disulphide of carbon, over which is a cooling apparatus which serves as condenser for the vapour of sulphide of carbon in distilling after the substances have been operated upon. Below the reservoir, one on each side, are two filters provided near the bottom with a movable and perforated shelf. Minerals are introduced into the filters upon the shelf through doors near the bottom, which are then closed and made air-tight. The liquid carbon disulphide is now admitted through a pipe at the bottom of each filter proceeding from the reservoir, and as the liquid rises it percolates through the minerals, dissolving out the bitumen, and when full flows out at the top through a pipe leading to a still, where the saturated liquid is distilled, the vapour of carbon disulphide ascending into the condenser, and the liquid sulphide of carbon as it condenses trickles into the reservoir beneath. The bituminous matters which remain in the still are drawn off by a cock at the bottom, and the disulphide which remains absorbed by the minerals in the filters is expelled by a current of steam. This apparatus is practically continuous, very little loss of the disulphide taking place at each operation, and as much as 12 p.c. of bitumen can be obtained, whereas only 7 or 8 p.c. could be had by distillation.

*Extraction of spices &c.*—Bonière has devised an apparatus for extracting the aromatic principles of various spices and other substances used for seasoning food by means of carbon disulphide. It is the same in principle as the apparatus already described, consisting of a series of wire-gauze sieves arranged one over the other in an air-tight case. The carbon disulphide is made to pass through the sieves which contain the substance to be operated upon, e.g. pepper, dissolving out the active principles, and as it reaches the top it flows through a pipe into a boiler. The boiler contains either salt, sugar, lactin, dextrin, saltpetre, or other material, according to what is under operation. The liquid is distilled in the boiler, which has some peculiarity adapted for this special purpose, at

140° to 150°F., by admitting steam into a kind of jacket, when the disulphide distils over and is condensed in a worm condenser, while the salt or sugar remains behind, retaining all the aromatic or acrid principles of the spice.

The pepper is not only exhausted by this plan, but the salt or sugar retains all the aromatic principles entirely free from smell or taste of the disulphide; the latter compound remains perfectly pure and may be used again for the same purpose.

Bergot has constructed an apparatus for rapidly determining the quantity of oil in seeds &c. by means of carbon disulphide. It consists of a glass vessel in the neck of which a cylindrical glass vessel is accurately fitted, and at the side in a tubulure is inserted a small air-pump. 50 grams of the finely ground seed to be examined are placed in the cylindrical glass vessel, and are covered with a diaphragm upon which 50 more grams are placed and covered with a second diaphragm. Carbon disulphide is now poured on until the seed is fully moistened, and after a few minutes a partial vacuum is made in the apparatus by means of the air-pump, when the pressure of the air drives out the disulphide and oil in solution into the vessel beneath. This is repeated until the carbon disulphide comes off colourless and leaves no oily stain on contact with filter paper. About 400 or 500 grams of carbon disulphide are sufficient to exhaust the above amount of seed.

The oily solution thus obtained is then heated in a saucer over a small water-bath, and as soon as the disulphide is all expelled the liquid is heated to boiling, allowed to cool, and is then weighed.

The combustion of carbon disulphide furnishes a sulphur dioxide, and it may be burned with the object of obtaining this gas in a lamp of special construction devised by Ckeandi Bey. The sulphur dioxide is useful as a disinfecting agent, is capable of rendering

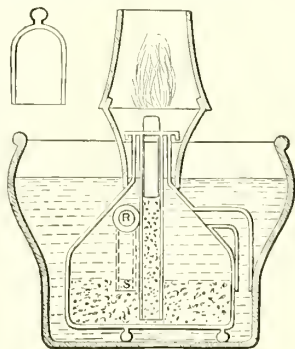


FIG. 4.

good service in the bleaching of silk and woollen goods, and it may also be used for bleaching sponges, straw hats, and many other objects. The lamp consists of an external vessel of tinned copper containing water; a second vessel containing the carbon disulphide stands in the water in the first vessel. To the

sides of the second vessel three siphons are fixed, which admit water into it from the first vessel on to the surface of the disulphide, the weight of the water forcing the disulphide up a central tube in which the cotton wick is placed. The flame can be regulated according to the height of the water in the first or external vessel, the pressure on the surface of the disulphide depending on this, and therefore the size of the flame.

When a room is to be disinfected the lamp is placed in the centre, and when lighted the door is hermetically sealed. When all the disulphide has burned it will, of course, be replaced by water through the siphons, and the lamp goes out of itself. The combustion proceeds with great regularity and without any danger. About  $5\frac{1}{2}$  lbs. are required for a room of 3,500 feet capacity (La Nature, 24, 117).

H. L. Greville has extracted with advantage the carbon disulphide absorbed in the purifiers of the gasworks. The lime used for this purpose, after being discharged from the purifiers, is introduced into a boiler capable of receiving a charge of several hundredweight, fitted with a perforated false bottom, pressure gauge, and an arrangement for admitting steam. The yield of carbon disulphide from one hundred tons of spent lime is about  $1\frac{1}{2}$  tons of disulphide of carbon. In addition to the value of the crude product thus obtained the lime remaining is, with a small addition of fresh lime, fit for further use in the purification of a further quantity of coal gas. As is well known, oxide of iron, after continued use in the absorption of sulphuretted hydrogen from coal gas, contains about 50 p.c. of free sulphur. The crude disulphide of carbon, obtained as described, can be used for the extraction of this sulphur, and the oxide which remains is revived, and is again fit for purifying purposes. The sulphur is recovered by distillation, and the carbon disulphide can be used over again (S. C. I, 2, 488).

The principal seats of manufacture in England are London, Manchester, and Ironbridge; in France, Paris, Bordeaux, and Marseilles. Germany has several manufactories, while within the Austrian dominions there is one in Galicia.

Deiss gives the following estimate of the cost of carbon disulphide when made by his plan:—

Sulphur in rolls, 733 kil. at 24 fr.	175-92
Charcoal, 160 kil. at 4 fr.	16-00
Labour, 2 men, per shift	18-00
Fuel, coke 28 hect. at 1 fr. 24 c.	31-25
Rectification, general charges	13-00
Cleaning the apparatus	20-00

274-17

Sulphur recovered, 300 kil. at 24 fr.

202-17

Produce, 433 kil. of disulphide, or the kil. costs nearly 47 c.

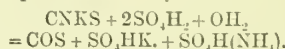
Carbon disulphide is produced at the rate of probably not more than 1,500 tons per annum in the United Kingdom; it is not imported, nor is it exported in any considerable quantity.

**Carbon monosulphide.** CS? A red powder obtained by exposing carbon disulphide to sun-

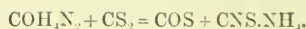
light. Insoluble in water, alcohol, turpentine, and benzene (Sidot, C. R. 69, 1,303; 74, 180; 81, 32).

**Carbon sesquisulphide**  $C_2S_3$ ? Löw, Z. 9, 173; 10, 20,  $C_2S_3$ ? Raub. C. C. 1870, 579. A red-brown powder formed by action of sodium on carbon disulphide.

**Carbon oxysulphide or carboxyl sulphide.** COS. Discovered by Than in 1867; occurs in certain hepatic waters or mineral springs. Prepared (1) by passing a mixture of carbonic oxide and vapour of sulphur through a hot tube;  $CO + S = COS$ .—(2) By the action of sulphuric acid upon potassium thiocyanate.

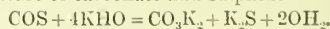


(3) By heating together sulphur trioxide and carbon disulphide;  $CS_2 + 3SO_2 = COS + 4SO_2$  (Armstrong).—(4) By heating urea with carbon disulphide in a sealed tube to  $110^\circ C$ .



The oxysulphide is given off together with hydrogen sulphide on opening the tube, and the latter is absorbed by passing through lead acetate (Ladenburg). For other modes of preparation v. WATTS' DICTIONARY.

**Properties.**—Is a colourless gas smelling like hydrogen sulphide, but with a slight aromatic odour. It is readily inflammable and forms with oxygen an explosive mixture. Water dissolves its own volume of the gas and acquires its characteristic smell and taste. A platinum wire heated to whiteness in the gas decomposes it into sulphur and carbonic oxide, the latter occupying the original volume of the gas. It has a specific gravity of 2.1046, and may be easily poured from one vessel to another. When burnt in air, it produces carbon dioxide and sulphur dioxide. With caustic alkalis it yields a mixture of carbonate and sulphide



It is liquefied at a pressure of 12.5 atmospheres and temp.  $0^\circ C$ . to a colourless, mobile, and highly refractive liquid, which dissolves sulphur and mixes with alcohol and ether, but not with water. If the pressure is suddenly released, solid flakes are deposited, and persist for some time (Hosvay, Bl. [2] 37, 294).

**CARBONADO** v. DIAMOND.

**CARBONITE** v. EXPLOSIVES.

**CARDAMOM OIL.** The volatile oil distilled from the seeds of any of the many species of cardamoms (called also grains of Paradise, Guinea grains, and Malaguetta pepper, all these names being used in a somewhat indeterminate sense) as *Anomum Malaguetta*, *Elettaria Cardamomum*, *Elettaria major* or *Granum Paradisi*, cultivated in Ceylon and Malabar, and to a small extent in Abyssinia. Sp.gr. of the oil 0.915. It is nearly colourless, of a strong aromatic smell and burning taste, and consists of a terpene b.p.  $170-178^\circ$ , terpinene and terpineol  $C_{10}H_{18}O$ , b.p.  $205-220^\circ$ .

Cardamoms come to this country as long-shaped triangular seed capsules, having three compartments all filled with small, rough, angular yellow-red seeds. The seeds yield about 5 p.c. of the volatile oil; they contain also a fixed non-drying oil of a rancid smell. The oil sometimes deposits crystals isomeric or identical with



hydrate of camphene. The smaller kind of cardamoms have been found adulterated with dried orange pips, detectable by close inspection.

**CARDINAL-RED.** Syn. *Acid Magenta*, *v.* **TRIPHENYLMETHANE COLOURING MATTERS.**

**CARDOL.** A non-volatile oil found in the pericarp of the Cashew nut, *Anacardium occidentale*.

**CARICIN.** An oil found in the seeds of the Papaw tree, *Carica Papaya* (Peckolt, Ph. [3] 10, 343).

**CARMINE.** The red colouring matter extracted from the cochineal insect. It is of somewhat variable composition, containing besides the colouring matter some organic matter from the insects and a little of the salt used to precipitate it from solution.

*Preparation.*—The powdered cochineal is boiled with water, the solution filtered or allowed to settle, and the colouring matter precipitated by addition of some salt, such as alum, stannous chloride, cream of tartar, Roman alum, &c. The precipitate is allowed to settle, and collected. Sometimes fish glue or white of egg is added before precipitation. Carmine is somewhat soluble in water and very freely soluble in alkaline solutions. The whole of the colouring matter is immediately precipitated by alum in the form of a lake.

In dyeing with carmine a mordant of alum or stannous chloride is used. Kienmeyer recommends the following mixture for printing on woollengoods; 14 kilos. gum, 17.5 kilos. cochineal lake, and 2.25 kilos. fustic lake, are mixed and warmed with 15 lit. water till the gum is dissolved, then 1 kilo. of oxalic acid and 1.75 kilo. acid sodium oxalate added, and the mixture allowed to cool, after which 2.25 kilos. sodium acetate are added. After printing, the fabric must be dried for a day or two, steamed under a slight pressure, and washed in a stream.

*Detection of carmine in cloth.*—Alcohol takes no colour from the cloth, but when it is boiled in solution of aluminium sulphate the solution turns red and the colour is unchanged by the addition of acid sodium sulphate.

The absorption spectrum of carmine in alkaline solution is remarkable, showing two dark bands between the lines D and E very similar to those of blood. Murexide and madder show no such bands. When wine is coloured with carmine the characteristic absorption bands cannot be seen unless more than 12 p.c. of the total colour is due to carmine (Gautier), but the adulteration can be detected by adding alum, when the colour changes to a rose tint.

It is said that the finest shades of carmine can only be obtained by working in direct sunlight.

**CARMINIC ACID** *v.* **GLUCOSIDES.**

**CARMOISIN.** Syn. for *Azorubin*, *v.* **AZO-COLOURING MATTERS.**

**CARMUFELIC ACID**  $C_{12}H_{20}O_{13}$ . An acid crystallising in thin plates formed by the action of nitric acid on oil of cloves (Muspratt and Dawson, P. M. [4] 2, 293).

**CARNALLITE.** A double chloride of potassium and magnesium  $KCl2MgCl_2 \cdot 12H_2O$ , found at Stassfurth, Prussia, in a thick layer under rock-salt beds, and accompanied by the minerals *Anhydrite*, *Kieserite*, *Tachydrile*, *Sylvite*, *Kainite*, and *Boracite*.

*Analyses by Rose.*

	1	2
Magnesium chloride . . .	31.46	30.51
Potassium chloride . . .	24.27	24.27
Sodium chloride . . .	5.10	4.55
Calcium chloride . . .	2.62	3.01
Magnesium sulphate . . .	0.34	1.26
Oxide of iron . . .	0.14	0.14
Water (by diff.) . . .	35.57	36.26
	100.00	100.00

Hammerbacher found traces of cesium, rubidium, and thallium in Stassfurth carnallite and in crystals resembling carnallite from a spring of Nauheim.

*Properties.*—Amorphous masses of a fatty lustre on fresh fracture, deliquescent and freely soluble, leaving a residue of iron oxide.

Used as a source of potassium salts and as a manure (*v.* **POTASSIUM**).

**CARNAUBA WAX** *v.* **WAX.**

**CARNINE**  $C_7H_5N_3O_3$ . A crystalline substance found in extract of meat, and obtained by treating the aqueous extract with lead acetate solution, and boiling the precipitate with water, when carmine separates out on evaporating the filtrate (*v.* Weidel, A. 158, 353; Schützenberger, C. R. 78, 493; Kruckenberg a. Wagner, C. C. 1884, 107).

**CARONY BARK** *v.* **CUSPARIA BARK.**

**CARRAGEEN.** *Carageen*, *Carragheen*, or *Carrageen*; Fr. *Garçon*, *Irish* or *Pearl Moss*. An alga (*Chondrus crispus*) found on all the western coasts of Europe and on the east coast of North America. In Ireland it is collected, dried, and bleached in the sun. Found in commerce as flat, dry, yellow-white pieces 2 to 3 inches long, usually branching, of a very faint odour and mucilaginous taste, swelling in water like gelatine. Almost completely soluble in boiling water; the solution sets to a jelly on cooling. Contains a high percentage of nitrogen, and is of value as a food in diseases of lungs and general weakness, usually taken dissolved in hot milk. It has also been applied as a size and for stiffening silk, also occasionally in making jellies.

Sometimes found largely adulterated with *Gigartina mamillosa*, which is less valuable and recognised by its stalked fruits and channelled stem (*v.* **ALGÆ**).

**CARRAWAY OIL** *v.* **OILS, ESSENTIAL.**

**CARRIAGE VARNISH** *v.* **VARNISH.**

**CARROT GUM** *v.* **GUMS.**

**CARROTIN.** The colouring matter of *Daucus Carota*. Found also in the leaves of plants and in the tomato. Crystallises in small red plates, insoluble in water, slightly soluble in alcohol, readily soluble in carbon disulphide. Composition unknown.

**CARTHAMIN.** The red colouring matter of the *Carthamus tinctorius* or safflower (order *Compositæ*) (*Rose Végétal*, *Rouge Végétal*, *Pflanzenroth*, but usually called carthamin, in French and German), a red dyestuff found in commerce as dry leaflets with brilliant peacock-green lustre and a strong smell of lemons. An inferior quality has a brown-red colour without lustre and an unpleasant smell.

*Preparation.*—The flower-heads of earthamus are placed in linen bags and kneaded in running water till no more yellow colour appears, then soaked in very dilute acetic acid and again

washed in running water. In this process the flowers lose about half their weight.

Stir with solution of sodium carbonate (16 lbs. soda to 50 gallons water and 100 lbs. safflower), let stand till clear, decant the liquid and press the residue. Add to the solution obtained as described 16 lbs. of fresh clear lemon-juice and a quantity of linen or cotton rags; all the colouring matter adheres to the rags. These are removed, pressed, and placed in a solution of sodium carbonate (10 lbs. soda to 40 gallons water). The rags are removed from the solution, which now contains all the pigment, this is then precipitated with just sufficient lemon-juice, filtered, and the precipitate dried on paper or porcelain plates. This process produces the finest quality of carthamin.

**Dyeing with carthamin.**—The earthamin is rubbed up with water and passed through a very fine sieve into a large volume of water. The article to be dyed is stirred with this solution till the desired shade is obtained, then removed, and dipped in a bath of alum or common salt; lastly, thoroughly washed and dried.

The best vegetable rouge is made from carthamin by the following process. Carthamin (or flowers of *Liatris scariosa*) is dissolved in very dilute solution of sodium carbonate. A quantity of very finely powdered chalk is added to the solution, and then just sufficient acid or lemon-juice to precipitate the colouring matter which is carried down by the chalk. The precipitate is filtered off, dried, and made into a paste with olive oil. This is called Spanish vegetable rouge.

The colour of carthamin is quickly destroyed by light. Its use as a dyestuff has been considerably restricted since the introduction of cochin and the saffranines. Its composition is  $C_{11}H_{10}O_2$  (v. SAFFLOWER).

**CÁRVACROL** v. CAMPHORS; also OILS, ESSENTIAL.

**CÁRVEOL** v. CAMPHORS.

**CÁRVOL** v. CAMPHORS.

**CASCARA SAGRADA.** The dried bark of the *Rhamnus Purshiana* (De Cand.), a small species of thorn-tree inhabiting the Pacific slopes of the Rocky Mountains. For botanical characters see Hooker (Flora Bor. Amer. 13); Prescott (Am. J. Ph. 1879, 165); Möller (Ph. [3] 14, 467); Moss (Ph. [3] 649, 19). *Cascara sagrada* has been long known as a cathartic to the Indians and trappers of California; but it has only recently been introduced into American and European medicine. Its physiological action is similar to the other and better known *Rhamnus Frangula* (Linn.), but the *Purshiana* is the more esteemed. Cf. Kennedy (Am. J. Pharm. 1885, 496).

Prescott has made a very complete proximate analysis of the bark. It contains *three resins*, which may be separated from one another by solvents, and a *crystalline compound*, together with *taunic acid, oxalic acid, malic acid, fixed oil, volatile oil, wax*, and a large proportion of *starch*. The crystalline compound melts and then sublimes just above 100°. According to Limoisin (J. Ph. [5] 6, 80), *Cascara sagrada* contains *chrysophanic acid*, and the resins obtained by Prescott are its decomposition products. *Emodin*, which occurs in rhubarb root together with a glucoside, yielding *chrysophanic acid*,

is also, according to Schwabe (Ar. Ph. 1888, 569), a constituent of *Cascara sagrada*. This compound, which is nearly related both in properties and constitution to *chrysophanic acid*, is of a darker orange-red colour (v. RUTBARR), and is probably the 'frangulin' of Wenzell (Pharm. Rundsch. 1886, 79). *Emodin* is also found in *Rhamnus Frangula* bark (Liebermann u. Waldstein, B. 9, 1775). *Cascara sagrada* has been further examined by Meier and Webber (Ph. [3] 18, 804) and Zeig (Ph. [3] 20, 173). A. S.

**CASCARILLA BARK.** The bark of *Croton Cascarilla*, or *C. Eluteria*, or 'seaside balsam,' a euphorbiaceous tree growing in the West Indies.

Duval obtained from it a substance, *cascarilline*  $C_{12}H_{10}O_6$ , which Alessandri (Ar. Ph. 220, 690) also isolated by extracting the bark with oxalic acid, and precipitating the extract with ammonia. This substance dissolves in hydrochloric acid, producing a rose-coloured solution, which changes through purplish-red, violet, and green to a sky-blue without the addition of water. Boehm (P. J. T. [3] 16, 366) finds in addition an alkaloid closely allied to cholin.

**CASCARILLA OIL** v. OILS, ESSENTIAL.

**CASEIN** v. ALBUMINOIDS.

**CASHEW GUM** v. GUMS.

**CASSAVA.** The name given to the starch obtained from the roots of several species of the *Manihot*, nat. ord. *Euphorbiaceæ*. Of these the most important is *Manihot utilisima*, a native of Central America, but now cultivated in the West Indies, Africa, and other tropical countries, yielding *bitter cassava*. Other species are *M. Carthaginensis* and *M. Aipi*, from which is derived *sweet cassava*. Gage, the Brazilian traveller (1625), mentions the cassava tree; whilst Humboldt found it to be in cultivation in South America, and the bread made of it to be the staple food of the natives. The plants grow in the form of a bush to a height of five or six feet. The tuberous roots form clusters of from three to eight in number, fourteen or fifteen inches long, four to five inches thick; they are large and fleshy, and sometimes amount to thirty pounds' weight on one plant. The tubers of the sweet variety are eaten when roasted or boiled.

To obtain the starch the root is ground to a pulp and pressed in bags. The residual mass consists of a mixture of albuminous matter, vegetable fibre, and farina, which is employed in making cassava bread, whilst the expressed liquor, after standing, deposits cassava starch. This starch is exposed to the heat of the sun, and forms what is known as Brazilian arrow-root or tapioca flour. It is from cassava starch that the article commercially known as tapioca is prepared by stirring it whilst in a damp condition upon hot plates. The starch granules for the most part burst during this operation, and a number of coagulated nodules results, in which form it is familiar in this country (v. TAPIOCA). The milky juice in the sweet variety is innocuous, whilst that in the bitter is highly poisonous, owing to the presence in it of hydrocyanic acid. Since, however, the active principle is volatile, it is easily dissipated by heat; so that in the case of the bread made from the residue, no deleterious effects survive the cooking of the cakes.

Examined under the microscope, granules of cassava starch show one rounded and one truncated end; the hilum is distinct, and placed near the rounded end. They vary in size from .0003 to .001 inch in length, and from .0003 to .0008 in breadth. No difference appears to exist in the character of the starch of bitter and sweet cassava; and in its chemical aspect it in no way varies from other starches.

**CASSEL EARTH, or VANDYKE BROWN, v. PIGMENTS.**

**CASSEL YELLOW.** *Oxychloride of lead.* A pigment also known as *Turner's Yellow*, *Montpelier Yellow*, *Mineral Yellow*, and *Patent Yellow*.

**CASSELMAN'S GREEN.** A pigment made by mixing boiling solutions of copper sulphate and an alkaline acetate.

**CASSIA.** The bark of *Cinnamomum cassia*, a tree belonging to the order *Lauraceae* or true laurels. It is grown in China, Java, &c. *C. Cassia* furnishes a bark which is much like cinnamon (*C. zeylanicum*), but thicker, coarser, stronger, less delicate in flavour, and cheaper; hence it is frequently used to adulterate cinnamon. The bark is stripped off the branches, when it rolls up in the form of quills. It is said to be preferred to cinnamon itself by some chocolate makers on account of its stronger flavour. The unopened flower-buds are also sold under the name of 'cassia-buds,' and possess similar properties to the bark. Other species of the genus afford aromatic barks, e.g. *C. Cutilawan*, native to Amboyna, the bark of which has a flavour of cloves; *C. iners*, a native of Malabar, of which also the seeds are used medicinally. The bark known as clove-cassia is obtained from *Dicypellium caryophyllatum*, which is also a tree of the laurel family growing in Brazil.

The employment of cassia as a sophisticant of the more esteemed and more costly bark of cinnamon when in the ground state may usually be detected by adding tincture of iodine to a decoction of the powder; when, since cassia contains more starch than cinnamon, the substance will turn blue; but, where inferior qualities of the true cinnamon have been examined, their constitution has approached that of the coarser bark of cassia, and this test has proved uncertain. *Cf.* O. Hehner (Analyst, 1879, 225-228).

Cassia bark is thicker, redder, stronger to the taste than cinnamon. The powder under the microscope exhibits a general resemblance to cinnamon, but it will be seen that cassia differs from cinnamon in its coarser structure, and especially in the greater size and number of its starch corpuscles.

Cassia yields by distillation an essential oil largely used in perfumery, especially for producing the scent in Brown Windsor soap (*v.* OILS, ESSENTIAL).

**CASSIA OIL v. OILS, ESSENTIAL.**

**CASSIA TORA or TAGEREY-VEREY.** This plant produces grains known in the East Indies, Arabia, and Japan as *Tora*, but which are known in Pondicherry and other parts of Hindostan as *Tagerey-verey*. It is regularly used as a component of the indigo vat in dyeing, apparently serving the same purpose as the bran-madder or molasses used in Europe.

The native dyers use the *Tagerey-verey* in the following manner. To dye about 200 yards of cloth, about 11½ lbs. of the grain are steeped in from 5 to 6 gallons of cold water, and then boiled for about four hours. The grains are swollen and softened by this treatment, and the water becomes thick and gummy. The whole of this is added to the indigo vat, and allowed to stand for fifteen hours, when the vat is ready to dye.

**CASSITERITE.** *Native stannic oxide*  $\text{SnO}_2$  v. TIN.

**CASSIUS, PURPLE OF, v. GOLD.**

**CASTILE SOAP v. SOAP.**

**CASTOR or CASTOREUM** (*Bibergeil*, Ger.). A name given to a secretion of the beaver (*Castor fiber*), contained in pear-shaped cellular sacs (found near the genital organs of the male and female animal), which are cut off and dried, to prevent the skin being affected by water. It is a substance analogous to civet and musk, and is of the consistency of thick honey and unctuous to the touch. The interior substance is solid, of a dark brown or black colour. It has a faint smell, softens when heated, but becomes brittle when cold. When chewed, it sticks to the teeth like wax. It has a bitter acrid taste, and a fetid, penetrating smell. Its fracture is shining, and when the substance is genuine it shows fragments of membrane indicating organic structure.

Three varieties are said to exist, the Russian, Bavarian, and American or Canadian, the first-named variety containing about 2 p.c. of the volatile oil, while the last contains only 1 p.c.

Wöhler obtained phenic and benzoic acids and salicine from it. Lehmann found bile in a fresh sample together with alkaline urates, sebates, and an albuminoidal substance. Laugier, Brandes, Batka, Bouillon, Lagrange, and Hildebrandt have also examined it. By extracting it with 6 times its weight of alcohol a colourless substance *castorin* has been isolated. Used in medicine and perfumery.

**CASTOREUM RESIN v. RESINS.**

**CASTORIN v. RESINS.**

**CASTOR OIL v. OILS.**

**CATECHIN v. CATECHU.**

**CATECHU.** This product, formerly called *Terra japonica*, is an extract prepared by boiling in water the wood, fruit, and leaves of certain plants growing in India and other Eastern countries. The decoction is evaporated to a syrup which solidifies on cooling, and forms a dark-brown or brownish-yellow earthy or resin-like substance. There are several varieties of catechu or catehu, bearing different names according to the country or plants from which they are obtained. The following are those principally employed by dyers and tanners: Bombay catechu, Bengal catechu, and Gambier catechu.

*Bombay catechu* is prepared from the wood and fruit of the catechu palm *Arca catechu*.

*Bengal catechu* is made from the twigs and unripe pods of *Mimosa catechu*.

These two varieties are similar in appearance, being sold in the form of large blocks of a dark brown colour, and showing a more or less lustrous fracture. They are imported from the East Indies, Java, Singapore, Pegu, &c.

*Gambier catechu*, also called *Cubical* and *Yellow catechu*, is obtained from the leaves of



the shrub *Uncaria gambier*, and occurs in commerce in the form of small cubes. It is of a paler and yellower colour than the other varieties, it is also more porous and exhibits a dull earthy fracture. It is imported from Batavia, Singapore, &c.

*Kino* or *Gum kino* is also a variety of catechu, but of less importance than the foregoing. It is furnished by *Bulea frondosa* and *Pterocarpus marsupium*, and occurs in commerce in irregular blocks of a deep reddish-brown colour, and showing a highly lustrous fracture. In Europe it is used in medicine or otherwise, but not for dyeing. All the above products have a strong astringent taste, are more or less soluble in cold water, and almost completely so in boiling water. All are rich in tannin matter, their aqueous solutions giving voluminous precipitates with gelatin and with sulphuric acid; with iron salts they give green colourations. Catechu is sometimes adulterated with sand, clay, blood, starch, &c. Good catechu should not contain more than 5 p.c. ash or more than 12 p.c. of matter insoluble in boiling alcohol.

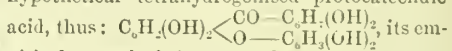
Catechu is mainly composed of two principles, Catechin and Catechu-tannic acid, together with a brown amorphous substance.

*Catechin*, the most important constituent, is best prepared from Gambier catechu by first dissolving out the catechu-tannic acid with cold water, and boiling the residue with water and filtering hot. On cooling, crude catechin separates out. It is purified by redissolving in hot water, boiling with animal charcoal to decolourise it, filtering hot and allowing to cool, these operations being repeated several times. It may also be purified by fractionally precipitating the hot solution with lead acetate. The last formed white precipitate is washed with water, and freed from lead by means of hydrogen sulphide; the residue is dissolved in boiling water and filtered hot. On cooling, pure catechin separates out. Etli's method of purification is to dissolve the crude catechin in dilute alcohol, filter, and remove the catechin from the filtrate by shaking up with ether; after distilling off the ether, the residue is dissolved in water and left to crystallise. The deep-red alcoholic solution, which remains after the removal of the catechin by ether, deposits on evaporating and cooling a red precipitate of *Catechin-red*.

Pure catechin is a white crystalline powder composed of minute silky needles. It melts at 217°C. and decomposes at higher temperatures, producing pyrocatechin and protocathechuic acid. It is only very slightly soluble in cold water, but readily so in boiling water, alcohol, and ether. Its aqueous solution is neutral to litmus; it gives a dark chrome-green precipitate with ferric chloride, or, if sodium acetate be present, an indigo-blue colouration instead. When dissolved in alkaline carbonates the solution rapidly absorbs oxygen and becomes dark red; by addition of an acid, a dark-red amorphous precipitate is produced of so-called *rubinic acid*, a very unstable substance. If caustic alkalis were the solvents employed, a dark-brown, almost black, compound named *japonic acid* is precipitated under similar conditions. Even aqueous solutions of catechin slowly undergo the same alteration by mere exposure to air, or it

may be at once effected by boiling with bichromate of potash. This property of catechin, of readily yielding, when submitted to oxidation, brown insoluble matters, forms the basis of the application of catechu in dyeing and printing.

When catechin is fused with potassium hydrate it is decomposed, forming protocathechuic acid and phloroglucin. This reaction, together with the composition of the anhydrides of catechin, leads Etli to consider that it contains the residues of 2 mols. phloroglucin and of 1 mol. of a hypothetical tetrahydrogenised protocathechuic acid, thus:



its empirical formula being  $\text{C}_{19}\text{H}_{11}\text{O}_8$ . In a later publication (Monatsch. f. Chem. 2, 547-557) Etli changes this formula to  $\text{C}_{19}\text{H}_{20}\text{O}_8$ , and considers the body referred to as having been a methyl derivative of catechin, to which latter he now gives the formula  $\text{C}_{19}\text{H}_{11}\text{O}_8$ . When catechin is heated to 140°C. with dilute sulphuric acid, it yields along with a red anhydride large quantities of pyrocatechin and phloroglucin, bodies which are also obtained by careful treatment of catechin with melting caustic potash. Etli therefore finally considers catechin to be derived from 1 mol. pyrocatechin and 2 mols. phloroglucin. The constitution and even the composition of catechin cannot, however, be regarded as definitely settled. Very numerous formulæ indeed have been assigned to catechin by different chemists, the discrepancies being due, according to Etli, to the different mode of drying adopted by the several experimenters, since catechin by heating or even standing over sulphuric acid loses not only water of crystallisation but a further quantity whereby it yields various anhydrides. Liebermann and Taubert consider catechin as crystallised from water to have the formula  $\text{C}_{19}\text{H}_{11}\text{O}_8 + 5\text{H}_2\text{O}$ , confirming it by the analyses of diacetyl-, dichloroacetyl-, and monobromoacetyl-catechin, all of which are crystalline compounds. When catechin is boiled with dilute sulphuric acid without access of air, or with alcohol containing hydrochloric acid, it is decomposed and yields a brown amorphous substance, called *catechurctin*, which according to Etli is identical with the tetra-anhydride of catechin ( $2\text{C}_{19}\text{H}_{11}\text{O}_8 - 4\text{H}_2\text{O}$ ) obtained by heating catechin for half a day with concentrated hydrochloric acid in a sealed tube at 160°-180°C. In cold dilute mineral acids catechin dissolves without alteration, strong acids, however, decompose it. Treated with concentrated sulphuric acid it gives a deep purple liquid. With concentrated nitric acid it yields a substance analogous to picric acid. With solutions of gelatin, tartar emetic, and starch, catechin gives no precipitate. An alcoholic solution of catechin diluted with water reacts with a solution of diazobenzene chloride, giving a reddish-brown crystalline precipitate (Etli) (Weselsky).

*Catechin-tannic acid* forms that portion of catechu which is soluble in cold water. According to Loewe it may be prepared in the pure state by boiling pulverised catechu with water and allowing the decoction to stand for several days. The precipitated catechin is filtered off, and the filtrate is evaporated to dryness; the residue is dissolved in alcohol and filtered, and any lime present in the filtrate is removed by

sulphuric acid; excess of the latter is then removed by lead carbonate, and a subsequent treatment with hydrogen sulphide removes any lead in solution. After precipitating various resinous matters with ether, the filtered solution is evaporated to dryness and the residue is dissolved in water. The solution is agitated with ether to remove traces of catechin, and on evaporation leaves pure catechu-tannic acid. According to Stenhouse and Groves the most convenient process for making pure catechin and catechu-tannic acid is the one founded upon the solubility of the former and the insolubility of the latter in dry ether.

According to Etti catechu-tannic acid is identical with the *mono-anhydride of catechin* ( $C_{21}H_{19}O_8 - H_2O$ ), and with *Catechin red*, and may be prepared by drying catechin for several days in a vacuum over sulphuric acid, and afterwards heating in an air bath to 127 C. It is also produced rapidly by boiling a sodium carbonate solution of catechin. Etti has prepared a *dianhydride* by boiling the mono-anhydride with dilute sulphuric acid, also a *trianhydride* by a similar treatment of catechin.

Catechu-tannic acid is readily soluble in water, and in alcohol, but not in dry ether. Its aqueous solution is precipitated by gelatin, and with tartar emetic. Ferric salts produce a greyish-green precipitate. With alkalis it forms soluble salts whose solutions rapidly oxidise on exposure to air and assume a reddish colour. It does not yield glueose on boiling with dilute sulphuric acid, and differs, therefore, in this respect from the tannic acid of gall-nuts. Catechu may contain from about 35 to 55 p.c. of catechu-tannic acid according to its source.

Dyers utilise the colouring properties of both catechu-tannic acid and catechin, whilst the calico-printer requires chiefly the catechin. Catechu is chiefly employed in cotton-dyeing for the production of browns, the cotton is impregnated with a decoction of catechu, and then passed through a boiling solution of bichromate of potash. Catechu is also employed for colouring and rendering less liable to rotting fishing-nets and sails: it is also used for tanning and as an astringent in medicine.

*Literature.*—Guibourt (J. Ph. [3] 11, 24, 260, 369; 12, 37, 183, 267). Pelliss (J. pr. Ph. 12, 162). Nenbauer (A. 96, 337). Nees and Seubek (A. 1, 313). Zwenger (A. 37, 320). Hagen (A. 37, 336). Van Delben & Kraut (A. 128, 285). Hlasiwetz and Malin (A. 134, 118). Schützenberger and Rack (Bl. [2] 4, 5). Stenhouse (Pr. 11, 401). Sace (A. 96, 337; C. R. 53, 1102). Gautier (Bl. 28, 147; 30, 567; C. R. 85, 342). Liebermann and Taubert (B. 13, 694). Etti (A. 186, 327; B. 11, 2266; Bl. [2] 24, 119; Loewe, J. pr. 105, 32, 75; Z. [2] 5, 538). Applications (Bl. Ind. Mulhouse, 12, 351, 373; 13, 291; 14, 186, 197; 22, 311; 34, 310; D. P. J. 2, No. 1, 1815). J. J. H.

**CATHARTIC ACID** *v.* SENNA LEAVES.

**CATHARTIN** *v.* SENNA LEAVES.

**CATHARTOGENIC ACID** *v.* SENNA LEAVES.

**CATHARTOMANNITE** *v.* SENNA LEAVES.

**CAT'S-EYE, AFRICAN,** *v.* CROCIDOLITE.

**CAYENNE PEPPER** *v.* RESINS.

**CEDAR OIL** *v.* OILS, ESSENTIAL.

**CEDAR CAMPHOR** *v.* CAMPHORS.

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**CEDRA.** *Chârat*, Fr. The fruit of a species of orange, citron, or lemon. The peel is very thick, covered with an epidermis containing a fragrant essential oil, used for flavouring preserves, also used whole for wet comfits, and cut in quarters for dry comfits. A liqueur is made from it by gathering the fruit before it is ripe, and grating the peel into brandy.

**CELESTINE** or **CELESTITE**; native Strontium sulphate (*v.* STRONTIUM).

**CELLULOID** is an intimate mechanical mixture of pyroxylin (gun-cotton or collodion-cotton) with camphor, first made by Hyatt, of Newark, U.S., and obtained by adding the pyroxylin to melted camphor, or by strongly compressing the two substances together, or by dissolving the constituents in an appropriate solvent, *e.g.* alcohol or ether, and evaporating to dryness. A combination of the two latter methods, *i.e.* partial solution with pressure, is now usually adopted.

The pyroxylin employed is generally the tetra- and penta-nitrated cellulose

$C_{12}H_{16}(NO_2)_4O_{10}$  and  $C_{12}H_{13}(NO_2)_5O_{10}$ , the hexanitrate (gun-cotton) being but seldom used on account of its explosive properties. Care is taken to prevent the formation of the hypernitrate by immersing the cellulose in only moderately strong nitric acid, or in a warm mixture of nitric and sulphuric acids. Thin paper, either in small pieces or in sheets, is immersed for about twenty minutes in a mixture of 2 parts of nitric acid and 5 parts of sulphuric acid, at a temperature of about 30°, after which the nitrated cellulose is thoroughly washed with water to remove the last traces of free acid, pressed, and, whilst still moist, mixed with the camphor.

In the process of Tribouillet and De Besancèlle the cellulose, which may be in the form of paper, cotton, linen, &c., is twice nitrated—first in the acid mixture employed in a previous operation, and secondly in a fresh mixture of 3 parts sulphuric acid, of 1.83 sp.gr., and 2 parts concentrated nitric acid containing nitrous acid. After each nitration the mass is subjected to pressure and is then carefully washed with water, to which, at the last, a small quantity of ammonia or caustic soda is added to remove the final traces of acid.

The impregnation of the pyroxylin with the camphor is effected in a variety of ways. The usual proportion of the constituents is 2 parts pyroxylin and 1 part camphor. In Tribouillet and De Besancèlle's process 100 parts of pyroxylin are intimately mixed with from 40 to 50 parts camphor, and moulded together by strong pressure in a hot press, and thereafter dried by exposure to air desiccated by calcium chloride or sulphuric acid. The usual method, however, is to dissolve the camphor in the least possible quantity of alcohol and sprinkle the solution over the dry pyroxylin, which is then covered with a second layer of pyroxylin, and the whole again treated with the camphor solution, the addition of pyroxylin and camphor solution being repeated alternately until the requisite amount of celluloid mixture is obtained. The mass which sinks together in transparent lumps is worked for about an hour between cold iron rollers, and then for the same period between rollers which can be gently heated by steam.

G G

The layer of celluloid surrounding the rollers is then cut away and again pressed, the resulting cake, which is now about 1 cm. thick, being cut into plates of about 70 cm. long, and 30 cm. broad; these are placed one above the other and strongly pressed together by hydraulic pressure at a temperature of about 70° for twenty-four hours. The thick cakes are once more cut into plates of the desired thickness, and placed in a chamber heated to 30°–40° for eight to fourteen days, whereby they become thoroughly dried and are ready to be fashioned into various articles either by being moulded whilst warm under pressure, or by being cut or turned. Occasionally other liquids, *e.g.* ether and wood-spirit, are used in place of alcohol as solvents for the camphor.

Celluloid may be readily coloured by means of various pigments, used either in solution or in suspension, and added to the mixture of pyroxylin and camphor before it is subjected to pressure. 'Marbled' celluloid is made by pressing plates of the differently coloured material together. Imitation tortoise-shell, used largely for the manufacture of combs, &c., is made by squeezing together plates of transparent yellow celluloid, with similar plates coloured with various shades of brown, &c.

Celluloid is highly inflammable, but non-explosive even under pressure; hence it may be worked under the hammer or between rollers without risk. It softens in boiling water, and may then be readily moulded or pressed into various forms. Its specific gravity varies slightly with its composition and with the degree of pressure to which it has been subjected: it is usually about 1.35. It appears to be merely a mixture of its components, since by treatment with appropriate solvents the camphor may be readily extracted, and on heating the pyroxylin burns away whilst the camphor volatilises. On account of its hardness and elasticity, and the ease with which it may be worked, polished, and coloured, celluloid is extensively used as a substitute for horn and ivory in the manufacture of knife-handles and combs, and for imitating amber, tortoise-shell, coral, malachite, &c.; *v. Böckmann, Das Celluloid*, Leipzig, 1880 (D. P. J. 235, 203; 239, 62; W. J. 1878, 1162; 1881, 949).

**CELLULOSE**, considered physiologically, is the main product of vegetable life. It is the preponderating constituent of all vegetable tissues, and essential to the cell as the structural unit. For while the synthesising activity of the cell is identified with its protoplasmic contents, its main function is the building up of non-nitrogenous substances, of which cellulose is the chief; elaboration of cellulose, in fact, is synonymous with growth.

By cellulose we understand the residue from the exhaustive alternate treatment of vegetable tissues with alkaline solvents and weak oxidants. No cellulose is isolated on the large scale except as the result of a chemical treatment, more or less drastic, of the fibrous raw materials; and all that we know of cellulose as a chemical individual results from the study of products so obtained. The typical cellulose is the substance of bleached cotton, the bleaching process, such as above described, removing the substances other than cellulose with which it is associated in the

plant. So obtained it is a white substance, translucent when viewed under the microscope, but more or less opaque in the mass. This appearance is a consequence of the peculiar form of the cotton fibre, a flattened thin-walled tube, the fibrille of which are membranously disposed. The reactions of cellulose are few. One of these may be mentioned here as being available for its identification, *viz.*, its property of giving a blue reaction with iodine solution in presence of or after treatment with dehydrating agents. The sp.gr. of cotton cellulose is 1.45. Its empirical composition corresponds to the formula  $\eta(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , by which, together with its constitutional relationships, it comes to be included in the group of the carbohydrates.

Cellulose contains mineral constituents, which remain as an ash after burning away the 'organic' portion. This ash usually takes the form of a complete skeleton, preserving the structural features of the original fibre. Though small in amount (0.1–0.2 % of the cotton), it is not to be regarded as an impurity, nor its presence as accidental. We shall not have occasion, however, to mention the mineral constituents of fibres otherwise than incidentally and in the aggregate, and in speaking of the fibre constituents we shall regard only the 'organic' components.

Another inorganic constituent, essential to the fibre under ordinary atmospheric conditions, is its *hygroscopic moisture* or *water of condition*. The quantity usually present in cotton is 6–7 p.c., varying necessarily with the temperature and the dew point. There are many considerations which lead us to regard this water as 'water of hydration.'

Cellulose is a typical *colloid*, and when fully hydrated takes a gelatinous form in which it is indistinguishable from other members of the group, *e.g.* silica and alumina. With the process of life there is a gradual and molecular dehydration of the tissues, and a progress from the gelatinous and 'amorphous' condition to the specialised forms of maturity. Dehydration of a vegetable tissue by exposure (after isolation) to air, but more especially by contact with alcohol, confers in a measure the properties which distinguish the fully elaborated celluloses. And *vice versa*, the rehydration of these celluloses by artificial means may be regarded as, in a limited sense, the reversal of the process of growth. On another view it is sufficiently evident that the commerce in water which is so prominent a feature and condition of plant life depends upon a bond of union much stronger than surface adhesion, in other words upon molecular attraction, and the relationships which subsist between plant and soil, upon the capacity for an indefinitely wide range of hydration changes which characterise their colloid constituents.

These theoretical considerations prepare the way for a brief account of the action of hydrolytic and dehydrating agents upon our typical cellulose.

**Ammonio-copper reagent** (*Schweitzer's Reagent*).<sup>1</sup> A solution of cupric hydrate in strong

<sup>1</sup> Although this reagent is known under the name of Schweitzer, its action appears to have been first studied by John Mercer (*Life of John Mercer*, London, 1886).



ammonia, prepared in any convenient way so as to contain no saline impurities, has a very remarkable action on cellulose. In contact with it the fibre gelatinises, and finally disappears in complete solution. From this solution various neutral precipitants, such as salts of the alkali metals, precipitate a blue, gelatinous, hydrated compound of copper oxide and cellulose; the combination, however, is easily resolved by washing with weak ammonia or by dilute acids. By dilution of the viscous solution the cellulose is precipitated; the precipitation, however, requires some days for its completion. It has been concluded from the effect of simply diluting that the cellulose is not actually dissolved in the solution, but an investigation of its osmotic properties proved the contrary (Cramer).

Acids dissolve the cellulose at the same time that they redissolve the copper oxide; the precipitate has the appearance of the gelatinous hydrate of alumina, and dries, similarly, to a hard horny mass. The precipitation of the cellulose by acids is complete; we may therefore conclude that its solution by the reagent is unattended by molecular transformations. Other celluloses, unlike that of cotton, are only incompletely reprecipitated, a portion remaining dissolved as a hydrated modification; from this we infer for them a different molecular aggregation. On adding lead acetate to the solution of cellulose in the ammonio-copper reagent a precipitate is obtained of a compound of cellulose with lead oxide, but in variable proportions. The compound ( $C_6H_{10}O_5 \cdot PbO$ ) is formed by the action of lead oxide on the above solution.

We are not aware that any explanation of the solvent action of this reagent has been attempted. We can only assume that the action of either constituent is specific. The aldehydic constitution of cellulose (*infra*) would account for the part played by the ammonia; that of the cupric hydrate is probably due to some particular relationship of its molecular weight in solution to that of the cellulose or cellulose hydrate formed. In confirmation of this view we may cite in anticipation the intensification of the hydrating action of solutions of caustic soda which results from the addition of hydrated zinc oxide.

*Technical application: 'Willesden' paper.*—When the solution in question is evaporated to dryness a gummy amorphous mass is obtained containing the cellulose intermixed with copper oxide. On the other hand, when the ammoniacal solution of copper oxide is evaporated on the surface of paper, calico, &c., after merely dipping in the solution, a green varnish-like compound of cellulose and copper oxide is left, coating the surface of each fibre, welding and cementing them together. This compound, in addition to having antiseptic properties, communicates water-resisting properties to the fabrics so treated. Two classes of these 'Willesden' goods are manufactured: (1) Rope cordage and netting are dipped in the solution and afterwards dried, the effect being a superficial conversion into the cupro-cellulose compound; (2) canvas, 'serim,' and paper, which are treated in the reel, being wound from one roller on to another, through the cuprammonia solution and over drying cylinders. Of the paper two

kinds are made, welded and unwelded. In the former two or more sheets, or welts, are rolled together, after being superficially gelatinised by the solution, into one compact homogeneous sheet. The product is a fabric of great durability, being scarcely affected by water even when heated in it for some weeks at a pressure of 60 lbs. per square inch (S. C. I. 1884, p. 121).

The action of the reagent above described is rather one of hydration than of hydrolysis, and the action of solutions of the caustic alkalis (potash and soda) may also be generally so described. Cotton cellulose is less susceptible to attack by these reagents than other forms of cellulose similarly obtained from the raw fibrous substances (*viz.* by treatment with either chlorine or bromine in presence of water and dissolving out the products of the reaction with boiling dilute alkaline solutions, or by processes strictly comparable with this, such as those employed by the textile bleacher and paper maker). While these solutions are practically without action on cotton cellulose through a wide range of temperature, the celluloses from Rhea, jute, Esparto, and even flax (bleached linen) are attacked and slowly converted into soluble products by boiling with dilute alkaline solutions. If this is true with the isolated celluloses it is *à fortiori* the case with the celluloses under the process of separation from combination; and when higher temperatures are employed, as in the pressure boilings of the papermaker and textile bleacher, the extent of the conversion, *i.e.* loss of weight, may be considerable. Other attendant results are also noteworthy. The drying of the fibres or fabrics after the processes of purification are complete must not be regarded as a mere desiccation. Those which are susceptible of this action of the alkalis give evidence of the alteration sustained, by hardening of the fibres when quickly dried; when the hydration has been considerable the contiguous fibres are agglutinated into wiry strands. A regulated dehydration by alcohol, or gradual drying, will be found to obviate the latter result. These considerations are of importance in their application to the 'finishing processes' which textile fabrics undergo after bleaching, and to the behaviour of paper pulps when dried on the machine. The greater bulk of cotton goods is dried by the direct application of heat by passing them over heated drums. Lizens, on the other hand, are stretched on frames in a loft, in which a medium temperature (25°) is maintained, and are pulled out by hand across the web during the whole time of drying. Also in the after-processes of beetling &c. the cloth is most carefully 'conditioned' by suitable application of water or exposure to the atmosphere. The highest qualities of papers also, instead of being rapidly dried on hot drums, are dried at only slightly elevated temperatures by passage of the web over a long series of hollow drums made of wire gauze, in the centre of which fans revolve in a direction contrary to that of the motion of the paper; or by the still more gradual process of exposure, in the form of sheets, to the ordinary atmospheric temperature (loft-dried paper). Another important point in connection with the 'conditioning' of paper is the alteration of tensions on dampening

the sheet, as in the ordinary process of printing, producing in many cases the well known effect of 'cockling.' Papers made from certain pulps, e.g. 'sulphite cellulose' (from wood), cannot be printed except by the dry process.<sup>1</sup>

The action of concentrated solutions of the alkalis at ordinary temperatures was first studied by Mercer. On treatment with solutions of caustic soda of sp.gr. 1.23-1.28 at the ordinary temperature, the cotton fibre undergoes a remarkable change; it swells, shrinks in length, and becomes transparent. The effect on cotton cloth may be described in Mercer's own words: 'I spotted bleached cambric with single drops of caustic soda solution (1.3 sp.gr.), and noticed that the central portion of each drop became semi-transparent and contracted; around this was a rim neither semi-transparent nor contracted, which evidently contained but little soda.' Many interesting particulars of these phenomena and suggestions of technical applications will be found in the *Life of Mercer* already cited; also in his specification of the patent in which he claimed the application of the results, and in the investigations of Crum (C. J. 1863) of the comparative properties and microscopic features of ordinary and mercerised cotton. We can only deal here with their more essential features. The linear contraction in the case of cloth is about 25 p.c.; the increase of strength (measured by the breaking strain on isolated threads) is about 50 p.c. After the treatment the cotton shows an increase of weight of 5 p.c., due entirely to excess of hygroscopic moisture over that of the untreated cotton. Experimental evidence shows that the action of the alkali is the result of its combination with the cellulose, in the molecular proportion, according to Mercer,  $C_{12}H_{20}O_{10}Na_2O$ , the combination being resolved on washing the fibre, water taking the place of soda to form the corresponding hydrate  $C_{12}H_{20}O_{10}H_2O$ ; the percentage increase calculated for this degree of hydration being 5.5 p.c. This water of hydration, though easily expelled on heating, is reabsorbed on exposure to the atmosphere. This fact confirms the view already advanced as to the 'molecular' character of the 'hygroscopic moisture' of celluloses. The 'mercerised' cotton, when exhaustively treated with alcohol for the removal of the excess of alkali, still retains a proportion of the latter corresponding to the formula  $2C_{12}H_{20}O_{10}Na_2O$  (Gladstone). The compound is easily decomposed by water and by carbonic acid.

These reactions of cellulose with the caustic alkalis vary considerably with the temperature of the solution, the variations being the inverse of those which are usual in chemical reactions, the effect being retarded by increase of temperature. With solutions of the strength above indicated the ordinary atmospheric temperature is most favourable. Weaker solutions, on the other hand, which are without action at this temperature, may be rendered

active by cooling. Mercer found that the greatest effect was obtained upon paper by immersion in a solution prepared by mixing caustic soda solution of 1.35 sp.gr. with 70 p.c. of its weight of snow or ice, the temperature of the mixture being below 0 F. It is remarkable that the addition of certain hydrated oxides soluble in caustic soda, such as the oxide of zinc, also increases the activity of the alkali. Thus a solution of 1.1 sp.gr., which has no sensible action on cellulose, becomes active when zinc oxide is dissolved in it in the molecular proportion of 1:4.

This remarkable modification of the celluloses resulting from the action of the alkalis has not received the wide technical application which it appeared at the time of its discovery to promise, not only by reason of the properties already noticed, but in 'the greatly augmented and improved powers of receiving colours in printing and dyeing' (Mercer, *l.c.*). The only applications of mercerised cotton which are at all noteworthy are in the preparation of piece goods for turkey-red dyeing and in the manufacture of calico-printer's blankets for machine printing.

The action of chloride of zinc in strong aqueous solution is similar to that of the caustic alkalis, and was included by Mercer in the patent specification above cited. The action of dilute sulphuric acid we find also included, and the changes which it and the other mineral acids determine must also be considered as changes of hydration, but in many respects they are different, and in some cases opposite, in character and effect.

Sulphuric acid at sufficient dilution (sp.gr. 1.35), nitric acid of sp.gr. 1.3, and concentrated hydrochloric acid, gradually disintegrate cellulose fibres at ordinary temperatures; the first action, on the other hand, is a toughening, accompanied by linear shrinkage. This action is applied in the laboratory for toughening filtered papers which are to be exposed to any considerable strain. The most convenient reagent is nitric acid (sp.gr. 1.3), the action of which is almost instantaneous (Francis, C. J. 1885, 183). Cellulose exposed to cold concentrated hydrochloric acid is converted in part into soluble derivatives, but the greater proportion into a friable modification resembling the original cellulose in all other essential features. This product was investigated by Girard (C. R. 81, 1, 105), and termed by him 'hydrocellulose,'<sup>1</sup> indicating that it is a hydrated derivative. The conclusions of Girard, however, appear to be doubtful, the evidence rather favouring the view that it is a dehydrated or condensed derivative, differing, however, but insensibly in empirical composition from the original cellulose (S. C. I. 4, 7).

A similar disintegration results from the exposure of cellulose to high temperatures. This has been the subject of special investigation by Scheurer and Grosseteste (B. Mulhouse, 1883, 62), who found that the fibre is unaltered by prolonged exposure to temperatures below and up to 150°; but at a few degrees above this point a very rapid disintegration occurs, shown

<sup>1</sup> The strength, as determined by the breaking strain, of a paper is further known to show considerable variations with variations in its hygroscopic conditions, and therefore in the hygrometric state of the air, a further evidence that the relationships of cellulose to water are molecular (vide Reports of the Papierprüfungs-Anstalt, Berlin).

<sup>1</sup> Altered by Witz to hydrocellulose.

by the loss of strength of fabrics so exposed. The action, moreover, was uninfluenced by immersing the fabrics in water, and heating, of course in closed vessels, to the same temperature ( $150^{\circ}$ - $160^{\circ}$ ). Oxygen, therefore, plays no essential part in the effect, and the point arrived at may be defined simply as the critical dehydration temperature of cellulose. The action is much accelerated and intensified by the presence of acids, even in minute quantity, the disintegration taking place at much lower temperature (Crace-Calvert: quoted in Crookes' 'Calico-printing').<sup>1</sup>

We have already treated of the action of sulphuric acid upon cellulose at such strengths that the changes determined are those of dehydration. At higher degrees of concentration the acid exerts a direct specific action, in fact combination takes place and the products are acid-ethers or *sulphates*. The reaction between the cellulose and acid molecules has been exhaustively studied by Hönig and Schubert (Monatsh. 6, 7; WATTS' DICTIONARY, new ed., article CELLULOSE). The formation of the sulphates is attended by resolution. On decomposing them either by treatment with water or alcohol, the corresponding carbohydrate molecules are regenerated, and these are seen to be more and more removed in character from cellulose, and more to approach the dextrins, the longer the action of the sulphuric acid and the higher its temperature ( $50$  to  $40^{\circ}$ ) in the first instance. When the action proceeds for a few seconds only and is then arrested, at the same time that the sulphate is decomposed, by treatment with water, a cellulose hydrate is precipitated, which might be described as a starchy modification of cellulose, or by the term *amyloid* applied by the earlier observers to the product. When the action is prolonged for some minutes, the carbohydrates similarly regenerated are soluble compounds forming, as already indicated, a transition series to the dextrins.

*Technical applications.*—We have to notice two industrial processes founded upon the reaction above described. Unsized papers, consisting of pure bleached cellulose (cotton), when plunged into sulphuric acid of sp.gr. 1.5 and rapidly and completely washed, are converted into what is known as *parchment paper*, a term which fitly describes the modification undergone by the paper substance, its chief external features being a considerable increase in toughness, transparency, and water-resisting power; the attendant results are a considerable linear shrinkage (20 p.c.), and a small loss in weight, due to conversion of a portion of the cellulose into soluble derivatives. The result may be summed up as a superficial conversion of the fibre into amyloid. The operations of plunging the paper into the acid and washing are now carried out upon suitable continuous machinery—i.e., the paper is treated in the web.

A second industrial process, based on the re-

action between cellulose and sulphuric acid, is its conversion into glucose. Bleached cellulose is dissolved in the strong acid, the viscous solution is diluted and boiled, the sulphuric acid is then removed by precipitation and the solution evaporated. The product is 'glucose.'

We have spoken of the reaction of the cellulose with sulphuric acid, in the first instance, as one of direct combination, with the formation of a sulphate and with elimination of water. Cellulose also combines with nitric acid to form the very remarkable series of cellulose nitrates, or pyroxylin, the highest members of which constitute the gun-cottons; but in this case the combination is usually brought about by indirect means, viz., by the action of mixtures of nitric and sulphuric acids. For although the combination is direct in the case of the acid of the highest concentration, the action is difficult to control, and the acid is diluted by the water formed and its action proportionately limited; the function of the sulphuric acid in the mixtures employed is to combine with this water and remove it from the sphere of action.

Thus far we have dealt with such compounds of cellulose (hydrates and ethereal salts) as have the simplest relationships thereto. We have dealt mainly with the typical cotton cellulose and have alluded only incidentally to the points of contrast of this with other celluloses. These differences are chiefly seen in their susceptibility to attack by hydrolytic agents, the action of which we may now briefly consider. Hydrolysis differs from hydration, as the term indicates, in involving a molecular resolution as the result of combination with water. It is true that, in certain of the hydrations already dealt with, there is a splitting up of the original substance; thus, in acidifying the solution of jute cellulose in the ammonio-copper reagent, a portion remains dissolved in the acid solution, whereas cotton cellulose is entirely reprecipitated. But there is no distinction in essential chemical features between the soluble and insoluble portions. We have to do with a soluble hydrated cellulose, just as we have soluble forms of alumina, ferric oxide, and silica. Contrast this, on the other hand, with the resolution by boiling with the dilute mineral acids of the cellulose isolated from fresh grass. Here a considerable proportion of the aldehyde fufural is split off from the cellulose, and the result is a hydrolysis in the strict sense of the term.

The hydrolytic agents of the laboratory are, as is well known, the dilute acids and alkaline solutions, and their action is powerfully aided by high temperature. The reagent may or may not combine as a secondary result with one or more of the products of the hydrolysis. Thus the fats—glycerin ethers of the fatty acids—are similarly resolved under acid and alkaline hydrolysis: the products are glycerine and fatty acid, when an alkali is employed it combines with the latter to form a soap. Hence the term saponification, and its generalisation in the language of science to include all such resolutions whatever the agent employed. Speaking generally, the celluloses isolated from mature plants are not susceptible of hydrolysis in the sense of saponification. Those, on the other hand, which are isolated from actively growing

<sup>1</sup> A practical application of these acid disintegrations is the process through which wool (and wool fabrics) are put for freeing them from the vegetable substances which find their way into the fleece. After scouring, the wool is immersed in a highly dilute sulphuric acid, the excess of solution removed, and the wool then dried in a hot chamber. The vegetable substances are disintegrated, and are then easily dusted out.



plants, are hydrolysed by boiling with dilute acids, and the characteristic product of the resolution is furfural. Towards alkaline solutions at high temperatures, the fully elaborated celluloses show a very considerable power of resistance, and when attacked they are rather hydrated and dissolved than hydrolysed and resolved. This resistance to the action of the alkalis, which is an aspect of the characteristic inertness of the group, is an important factor of their relative values in the arts, as we shall presently see. It will be seen to be implied in the empirical definition of cellulose given at the commencement of this article. We shall find, however, that when to hydrolysing conditions that of oxidation is added, cellulose is attacked and structurally modified, more or less profoundly, according to the degree of action. Such oxidations are of great importance technically; more particularly those of which the products are so related to the original cellulose that they may be regarded as derivatives.

**Oxycellulose** (Witz, Bl. S. I. Rouen, 10,416-11,189). When cotton is subjected to the action of a solution of bleaching powder with access of air—e.g., when a piece of bleached calico is moistened with the solution and exposed to the air, the oxidation causes a notable change in the composition of the fibre substance, and this is accompanied by disintegration more or less profound according to the degree of oxidation. The following percentage numbers indicate the composition of the resulting oxidised derivatives of cellulose and the rate of progress of the oxidation:

	12 hours' exposure			22 hours' exposure	
C	43.78	43.47	.	.	43.00 42.90
H	5.85	6.13	.	.	6.28 6.18
O	50.17	50.40	.	.	50.72 50.92

Other oxidising agents produce similar results: thus the frequent 'tendering' of cotton goods in the process of open lime boiling (*v. BLEACHING*) has been shown by Witz to be a local conversion into oxycellulose due to the action of the air jointly with the alkaline solution; 'active oxygen' in presence of water has a similar and rapid action, and even by exposure to air and light, cellulose is slowly converted into these oxidised derivatives. The distinguishing features of these compounds are as follows. They are coloured bright yellow by solutions of the caustic alkalis. On adding cupric oxide (Fehling's solution) and warming, the oxide is rapidly reduced and is deposited upon the fibre in such a way as to produce the effect of an orange-red dye. The oxycelluloses have a powerful attraction for the basic colouring matters, and this property enables us to diagnose very exactly the condition of oxidation of the substance (cellulose) of textile fabrics, as also to detect any excessive local oxidations. Another feature of the oxycelluloses is that they are proof against the action of all known reducing agents. These are important points for the bleacher to bear in mind; more particularly perhaps, in regard to fabrics intended for dyeing, since excessive local action of the bleaching agent, even where it does not reach the point of tendering the fabric permanently, modifies the dyeing capacity of the fibre. The cotton dyer has the not uncommon experience of stained goods; the stains not visible

in the bleached cloth, but 'turning up' during the dyeing of the goods. The reappearance of such 'stains' after discharging and redyeing is evidence that the cloth is in those places over-oxidised, and therefore, as it were, permanently mordanted.

Another remarkable property of these derivatives according to Witz (*l.c.*) is their attraction for vanadium compounds, which are withdrawn by the oxycellulose from aqueous solutions containing so microscopic a proportion as  $\frac{1}{1,000,000,000}$ th of the element (in the form of chloride).

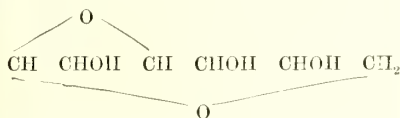
**B. oxycellulose.**—Another oxidation, technically perhaps less interesting, but also throwing light on these problems of the constitution of cellulose, is that produced by dilute nitric acid at or near the boiling point. On digesting cotton with the acid of sp.gr. 1.2-1.3 at this temperature, a considerable quantity of oxalic acid is formed, and after prolonged digestion a residue remains amounting to about 30 p.c. in weight of the original fibre, which yields but very slowly to the action of the acid. This substance, when thrown upon a filter and washed, combines with the water to form a gelatinous hydrate. It dissolves in dilute alkalis, but without forming a stable compound with the base. Its elementary composition is expressed by the formula  $C_5H_7O_{11}(C\ 43.1-H\ 5.3\ p.c.)$ . Treated with a mixture of concentrated sulphuric and nitric acids, it dissolves, and on pouring the solution into water the compound  $C_5H_7O_{11}(NO_3)_3O_{13}$  separates as a white flocculent precipitate. These oxycelluloses, distinguished from the preceding group by the prefix  $\beta$ , stand, in regard to many of their properties in very close relationship to the group of pectic derivatives, which are oxidised derivatives of cellulose formed by 'natural' processes (*v. C. S. J.* 1883, 22).

The actions of other oxidising agents upon cellulose have been but little studied. Chromic and chloric acids were employed by Witz as topical oxidants, forming oxycellulose, and producing designs which could be developed by dyeing out in a bath of any basic colouring matter. Such a process, however, although ingenious and a striking illustration of the results of his researches, has not led to any technical development, the colours produced lacking fastness. The oxidising mixtures employed in aniline-black printing, also convert the cellulose into oxycellulose, and the simultaneous oxidation of fibre and colour-base is no doubt a factor of the exceptional fastness of the black. The oxidising action of ferric compounds in presence of light is also worthy of mention, as it received at the hands of Mercier an interesting application to the production of photographic pictures upon cellulose fabrics.

Contrasted with these oxidations of cellulose in acid or feebly basic solutions are those of alkaline solutions of the permanganates and hypochlorites, which have been found to yield as oxidation products acid bodies isolated in the form of a synnp, their properties indicating that they are products of the hydrolysis accompanying the oxidation: *i.e.* acids of the carbohydrate series of lower molecular weight than cellulose.

*Anhydrous oxidations.*—Cellulose heated at high temperatures with very concentrated solutions of potash (which may be considered as an anhydrous action) is converted into oxalic and carbonic acids. Such a process has been employed industrially for the production of oxalic acid (Dale). Treated with chromic anhydride in presence of concentrated sulphuric acid it is entirely resolved into gaseous products, viz. carbonic anhydride with a variable small proportion of carbonic oxide. The resolution being complete, a process for the ultimate analysis of cellulosic substances has been based upon this decomposition. The volume of the evolved gas being measured, the proportions of carbon may be calculated therefrom, the quantity in unit volume being independent of its composition in regard to  $\text{CO}_2$  and  $\text{CO}$ , since these gases have the same volume (C. N. 52, 207; C. J. 53, 889).

*Constitution of cellulose.*—Although this aspect of our subject involves purely scientific considerations, it cannot be said to be without practical bearings. Without attempting to discuss experimental evidence, we may define it as a saccharocolloid (*v.* Kohlenhydrate, B. Tolleus),  $\text{C}_6\text{H}_{10}\text{O}_5$ , of which the typical constitutional unit or  $\text{C}_6$  group might be formulated as under:—



an expression which fairly generalises the reactions of cellulose.

**Physiology of the compound celluloses. (Vegetable fibres.)** While the simplest form of vegetable life is the cell, and the cell is, moreover, the universal originating unit, we observe as we ascend the scale of plant organisation an increasing variety of differentiations of this simplest structural unit graduating into the fibres and vessels of the stems of the higher flowering plants. Careful observation will show that it is to the presence of such elongated cells as warrant the designation 'fibre' that these stems mainly owe their powers of bearing strains and resisting fracture. The uses to which these fibres are put in the arts obviously depend upon the same characteristics of form, as well, of course, as the nature of the fibre substance. So too the anatomy of fibrous stems is necessarily a main factor of the processes by which they are treated for the isolation of the fibres. We must here except from the general anatomical view we are about to take the most important of the vegetable fibres, viz. cotton, which as a seed hair is distinct physiologically, and differs structurally from all other fibres employed for textile purposes.

The 'ultimate' fibre is a hollow tube, the walls being thin and membranous; it is attached at one end to the testa of the seed, the other being free, and there is no adhesion of the fibres to one another. The preparation of the textile fibre involves therefore only a mechanical treatment, and that of the simplest kind, for separating it from the seeds. The other vegetable fibres employed in the arts are without exception

constituents of complex structures (stems and leaves) which require a more elaborate mechanical operation for their separation, in addition in many cases to a preparatory chemical treatment.

The fibres of stems are arranged according to the two main structural types of growth, the exogenous and endogenous. In the exogenous stem of annuals (dicotyledonous) they constitute a localised tissue, the bast, which is an annular ring external to the wood and beneath the cortex. In the endogenous stem the fibres proper (bast fibres) are generally aggregated together with vessels into bundles known as fibro-vascular bundles, which are scattered more or less irregularly throughout the cellular matrix.

In regard to the leaf, the two great divisions of the phanerogams are also contrasted; the fibro-vascular bundles of the former are not only irregularly disposed, but interlaced (reticulate venation), whereas the leaves of the typical monocotyledon are characterised by a parallel arrangement of the bundles, and fulfil, therefore, a necessary condition of separation for textile purposes. Fibres of this class are amongst the most useful that we have. There is a distinction to be noticed, though rather of a technical than anatomical nature, between the vegetable fibres and 'fibrous substances.' By the former we understand isolated bast fibres or fibro-vascular bundles, such as can be *spun* into a continuous length or yarn. A fibrous substance is of course any vegetable structure containing fibres. Many of these do not admit of being economically treated for the isolation of a textile fibre, but on the other hand are resolved by suitable chemical treatment into a fibrous mass or *pulp*, available for paper making. Many of our most valuable raw materials for this industry are of this nature. We may further distinguish according to the above classification, (1) exogenous bast tissues, such as those of the *Adansonia* and *Broussonetia* (paper mulberry) and entire stems (woods), and (2) endogenous stems (straws and bamboo), and leaves (*esparto*). In this more miscellaneous group also we should include the refuse from the preparation of textile fibres, such as the root ends of jute (butts), the waste from the flax scutching process (*infra*), &c.

We have already excepted the cotton fibre from the above classification, indicating a structural as well as a physiological distinction from other textile fibres. These are in fact always obtained and spun in the form not of *ultimate* fibres but of bundles of these. The ultimate bast fibre is also a hollow tube, but more or less thick walled and with tapering extremities; in section it is seen to be cylindrical or polygonal. The dimensions are remarkably uniform for the bast of any given plant or species, but exhibit wide variations from species to species. Thus the average length of the bast cell of jute is 3 mm., and of flax 28 mm. The textile 'fibres' are aggregates of these ultimate fibres, and it is convenient to employ for them the special designation of *filament*. This complex spinning unit varies in the number and degree of cohesion of the constituent fibres. These variations even in the same plant or species are very considerable, but more so as we pass from species to species. Expressed in another way the textile

fibres vary very much in regard to fineness and divisibility of the filaments. These, it is scarcely necessary to say, determine in a very important sense their spinning qualities. The nature of the fibre substance is a self-evident factor of the mechanical properties of the filaments; and lastly, though less obviously, the length of the *ultimate fibre*, which greatly influences the strength and durability of the yarn.

To the spinner the chemical composition and properties of the fibre substance may appear of altogether secondary importance; but they are obviously of first importance in regard to the application of the yarn, as of the goods woven from it. Supposing them put into use without further preparation, the durability of the fabrics will depend upon their resisting the disintegrating action of air (oxygen) and water, reinforced by heat and light. But a large proportion of the textile fabrics of commerce are supplied to the consumer in the bleached state, the process of bleaching consisting in the removal by a more or less drastic treatment with reagents of those fibre constituents to which the colour of the raw material is due. These processes being the subject of a special article, we shall not require to deal with them at all in detail. The principles underlying them, however, have a close and obvious connection with the properties of cellulose, and the relationships subsisting between the cellulose of the vegetable fibres and the non-cellulose constituents with which each is associated in the plant, and from this point of view we proceed to give a short account of the

*Chemistry of the compound celluloses.*—There are many reasons for regarding cellulose and the non-cellulose constituents of vegetable tissues and fibre substances as united chemically. Taking cellulose as the constant, the basis of our classification of the compound celluloses will be the nature of the non-cellulose, the characteristics of which are as distinct as they are general (Sachsse, *Farbstoffe*, &c., p. 143). Physiologists recognise three 'modifications' of cellulose in the plant, and these we term compound celluloses. We shall find the distinguishing chemical features of the three groups of compound celluloses as well marked as their functional correlations, and the corresponding classification has a 'natural' in addition to its chemical significance. We shall consider first the group which is of least, because of only incidental, importance in relation to our subject.

**Adipocelluloses.** The protective tissues of plants, which are, moreover, cellular rather than fibrous, viz., cork and cuticle, are composed of a substance of marked water-resisting characteristics. In this property as well as in empirical composition the cuticular substance designated *cutose* by Fremy resembles many of the waxes. The following percentage numbers are the results of the analysis of the cuticle of the apple purified from wax and adventitious matters—C 73.66; H 11.37; O 14.97.

Cork is not a simple substance but contains a number of products, wax, proteid residues, and tannins, &c., associated with the matrix or skeleton substance, which is of the nature of *cutose*. Both *cutose* and cork yield a residue of cellulose when treated with special reagents

(sulphites) for the resolution of its union with the wax like non-cellulose. The latter<sup>1</sup> is resolved by boiling with strong solutions of the alkalis into two fatty acids, a solid acid designated *stearoctic* and a liquid called *oleoctic acid*. The investigation of these cuticular substances has not been sufficiently extended to warrant our entering into further detail in regard to their composition and properties. We may regard them as compound celluloses resolved by alkaline saponification into cellulose and a mixture of fatty acids of peculiar properties, but altogether unknown constitution. They may be conveniently grouped under the term *adipocelluloses*, which broadly expresses their chemical relationship. As regards their distribution, they occur chiefly in the epidermal and cortical tissues of leaves and stems, but the observations of Fremy lead to the conclusion that they are by no means confined to these, and there is evidence of their presence, if only in minute proportions, in the fibres themselves; but their occurrence, chemically speaking, may be regarded as adventitious, the fibre substances belonging to essentially different classes of compounds. These *adipocelluloses*, moreover, in all the technical applications of vegetable materials which come within the province of this article, have to be got rid of. When the fibres themselves are isolated this is accomplished for the most part by the mechanical processes of preparation, scutching, hackling, &c. When, however, the tissue intervening between the fibres and the cortex or epidermis is of small extent the separation is never complete. In flax, for instance, residues of the epidermal tissue remain associated with the fibre, and the relative difficulty of attacking these substances by chemical means is a factor of the laborious process of bleaching linen goods. In isolating the so-called New Zealand flax much greater difficulty is experienced. This fibre consists of the fibrovascular and other fibre-bundles of the sword-shaped leaf of the *Phormium tenax*, and these are in such close and intimate contact with the epidermal tissues that their isolation is always very incomplete. In those raw materials of the paper-maker which consist of the stems and leaves of monocotyledons (straw and esparto), the epidermal *adipocelluloses* constitute a sensible proportion. They are resolved in this case by chemical means, which require to be much more drastic in consequence. The fibrous portions of these materials, on the other hand, are made up of a compound cellulose belonging to the next group which we shall have to consider, an important characteristic of which is the comparative ease with which they are attacked and resolved by alkalis. Although, therefore, the connections of these cuticular celluloses with the fibres are for the most part only indirect or incidental, we see in the typical instances above cited, that they have to be taken into account in relation to a great number of the treatments of cellulosic raw materials, both mechanical and chemical.

**Pectocelluloses.** This, the second division of the compound celluloses, is characterised by

<sup>1</sup> According to Fremy it is the *cutose* itself which is so resolved, but the author's experiments have always yielded a residue of cellulose.



the non-cellulose constituents belonging to the group of *pectic* substances.

In composition they are more complicated than the celluloses, and they contain less carbon and more oxygen. In this and in many of their properties, they resemble the  $\beta$ -oxycelluloses above described. Generally they yield gelatinous hydrates, and under the action of hydrolytic agents they undergo a succession of changes resulting in the conversion of the comparatively inert members of the series pectose and pectin into highly acid derivatives, such as pectic and metapectic acids, bodies which, in addition to being acids, have properties indicating the presence of aldehydic groups.

The typical pectocellulose is the flax fibre. The purified bast of a Russian flax was found by Kolb to contain C 43.7; H 5.9; O 50.4.

On boiling with dilute alkaline solution about 20 p.c. of its substance is readily converted into soluble derivatives, of which a considerable proportion is a body identical with Fremy's pectic acid (C = 42.0 p.c.; H = 4.8, i.e.  $C_{12}H_{22}O_{15}$ ). The fibrous residue from an exhaustive treatment with alkaline solutions, amounting in most flaxes to about 75 p.c. of the original weights, is a practically pure cellulose. In this experimental account of its constitution we disregard such adventitious admixtures as cuticular tissue (adipocellulose) and wood or 'spit' (lignocellulose), the influence of which may be calculated and eliminated from the result; but the presence of these in commercial flax introduces complications of very great moment in regard to the spinning of the fibre and the bleaching processes to which flax goods are subjected.

**Lignocelluloses.** As the name indicates, this group comprises the substance or substances of which woody tissue is made up. The simplest type of these bodies is the *jute* fibre, the lignified bast of a herbaceous annual (*Corchorus Tiliacea*), cultivated on an enormous scale in India.

The elementary composition of the purified bast is expressed by the following percentage numbers:

		C	Ce.	$C_{12}H_{22}O_{15}$	
C	47.0-48.0	.	.	.	47.0
H	5.9-5.7	.	.	.	6.0
O	47.1-46.3	.	.	.	47.0

On Sachsse's view (Farbstoffe &c., p. 115) it is a compound of

Non-cellulose (lignin)  $C_{12}H_{10}O_9$  (55.5 p.c.) 25 p.c.<sup>1</sup>  
Cellulose . . .  $C_6H_{10}O_5$  (44.4 " ) 75 "

The cellulose isolated from the fibre, as a product of chemical resolution, differs, however, from the typical cellulose in empirical composition, viz.  $3C_6H_{10}O_5.H_2O$ , and in being more readily attacked by oxidising and hydrolytic agents. While the whole molecule or compound cellulose agrees in certain typical reactions with cellulose itself, e.g. solubility in the ammonio-cupric reagent, formation of explosive nitrates and soluble sulphates, it exhibits equally marked differences, as follows. It is coloured brown by iodine, bright yellow by solutions of the salts of aromatic bases, deep red by phloroglucin in presence of concentrated HCl. The solution in the

Schweitzer reagent is only partially reprecipitated by acids, precipitate same as original; the explosive compounds with nitric acid are yellow, and their formation is attended with partial conversion into soluble derivatives in proportion to the temperature and the duration of contact with the acid mixture. It is much more susceptible of attack by oxidising and hydrolytic agents. Of the latter, boiling alkaline solutions (caustic soda of 2 p.c. Na<sub>2</sub>O) dissolve 10-15 p.c. of the weight of the fibre, but without any structural change; acid solutions (H<sub>2</sub>SO<sub>4</sub> 5 p.c.) dissolve 15-30 p.c., according to the duration of the action. The characteristic final product of the acid hydrolysis is the aldehyde furfural. The attendant changes in the residual fibre are similar to those described in the case of cellulose. Where the hydrolysing action is supplemented by oxidising or reducing conditions, a resolution of the lignocellulose is brought about. Thus, when digested with dilute nitric acid (5-10 p.c.) at 60-80°, the non-cellulose is entirely, and, as might be expected, the cellulose is in part, converted into soluble products. The solution is yellow, and contains a derivative of complicated composition  $C_{23}H_{40}(NO_2)_2O_{23}$ , a highly acid body which dyes animal fibres to a gold shade, and forms salts with the earthy bases ( $C_{23}H_{42}(NO_2)_2O_{23}M'$ ). It is worthy of note at the same time that the presence of urea prevents this specific action of nitric acid, diverting it into one of simple hydrolysis, as with the stable mineral acids (H<sub>2</sub>SO<sub>4</sub>, HCl). On the other hand, sulphurous acid resolves the lignocellulose molecule, as also the bisulphites and sulphites of the alkalis and alkaline earths. The temperatures necessary for the isolation of cellulose are with sulphurous acid (7.5 p.c. SO<sub>2</sub>) 90-100°, with bisulphites (4 p.c. SO<sub>2</sub>) 110-150°, with normal sulphites (4 p.c. SO<sub>2</sub>) 170-180°, the increase of temperature corresponding with the diminution of hydrolytic power by progressive neutralisation of the acid. It is scarcely necessary to state that the pressures involved require the use of sealed apparatus for these digestions. The hydrolysis is aided by the combination of the reagents with the soluble derivatives, which are aldehydic in character, preventing the reversal of the actions which would otherwise occur as the higher temperatures are gradually reached. These reactions receive important technical applications which will be subsequently described.

But the most characteristic reactions of this compound are those with the halogens. Iodine is absorbed, as already stated, but the resulting brown-coloured compound is not more stable than the iodide of starch. Under uniform conditions the quantity taken up is approximately constant, and the reaction may be applied to the approximate estimation of the proportion of a lignocellulose in admixture with a cellulose. Bromine attacks the fibre in contact with water, forming ill-defined compounds, which are dissolved by alkaline solutions. The operation once or twice repeated eliminates the whole of the non-cellulose; the resulting cellulose amounts to 72-75 p.c. of the weight of the fibre. Chlorine does not act upon the dry fibre, even when the temperature is raised to 100°, but in pre-

<sup>1</sup> Recent researches (C. J. 1889, 195) have shown that this non-cellulose is a complex molecule containing (a) a ketone  $C_{12}H_{10}O_9$  transitional to a quinone; (b) a furfural residue; (c) an acetic residue.

<sup>2</sup> Tollens has obtained xylose as a direct product of the hydrolysis (Ber., 1883, 1045).

sence of water combines rapidly at ordinary temperatures with evolution of heat. The chlorinated derivative is yellow, soluble in alcohol, and is precipitated from the solution by water in flocks. Its composition is expressed by the empirical formula  $C_{10}H_7Cl_2O_6$ . It gives with sodium sulphite solution a characteristic magenta colouration. Boiled with the solution the chlorinated derivative is entirely dissolved and a residue of cellulose remains, consisting of the now disintegrated fibre elements or cells. This process is the simplest and most rapid

method of estimating the cellulose in this as in all other lignocelluloses. The chlorinated derivative of the non-cellulose is aromatic in character, and resembles the products of chlorination of the trihydric phenol, pyrogallol.

The results of a proximate analysis of the raw fibre substances, according to the ordinary method of successive exhaustion with various solvents (ether, alcohol, and water), are sometimes of value. In the subjoined table we give a typical selection of such results compiled from Dr. Hugo Müller's *Pflanzenfaser*:

—	Seed Hair	Dicotyledonous				Monocotyledonous	
		Bast fibres				Stems	
		Cotton	Flax	Hemp	Rhea	Jute	E-parto
Cellulose <sup>1</sup> . . . . .	91.35	81.99	77.13	75.83	63.76	48.25	47.69
Wax . . . . .	0.40	2.37	0.55	0.20	0.38	2.07	1.93
Aqueous extract . . . . .	0.50	3.62	3.45	6.29	1.00	10.19	10.05
Moisture . . . . .	7.00	8.60	8.80	8.74	9.86	9.38	11.38
Ash . . . . .	0.12	0.70	0.82	2.87	0.68	3.72	3.20
Pectous substances <sup>2</sup> . . . . .	—	2.72	9.25	6.07	21.32	26.39	26.75

The chemical characteristics of the compound celluloses have been sketched in sufficient detail for the elucidation of the processes to which they are subjected, and we proceed to consider such of these as come within the scope of this article. They may be divided into two groups: (a) chemical processes natural and artificial, auxiliary to the isolation of textile fibres (filaments); (b) the processes of the paper-maker by which he resolves his raw fibrous materials into ultimate fibres (pulp).

(a) The purpose of these treatments is to disintegrate the cellular tissue in which the fibres are, as it were, imbedded, and thus facilitate the mechanical operation of separating the fibres. Of this group of processes the treatment of flax is typical. In the mature flax stem the annular ring of fibres, amounting to about 20 p.c. of the total weight, is cemented together with the external cuticular tissue and the wood which constitutes an internal cylinder, into a coherent whole. The cellular tissue to which this adhesion on either side is due is composed of a cellulose which is much more susceptible of hydrolysis than any of those compound fibre-celluloses above described, and by exposing the stem therefore to some hydrolytic agency, it may be so far disintegrated as to free the fibres, so that in the breaking and beating of the scutcher the wood and cortex are broken up and stripped with the minimum waste of fibre. The simplest system of preparation is that of dew retting, which consists in exposing the 'straw,' thinly spread upon grass, to the influence of the weather, until upon trial the fibre parts easily from the wood or 'sheave.' An exposure of several weeks' duration is necessary. The flax produced upon this system is of low quality; notwithstanding which the method is still largely practised in Russia, and to some extent also in Belgium.

<sup>1</sup> Determined by exhaustive treatment with bromine water and boiling dilute ammonia for elimination of non-cellulose. The result is calculated on the air-dry substance.

<sup>2</sup> These include the substances dissolved away by the above treatment; they are calculated by differences.

The latter country is distinguished on the other hand for the exceptional quality of the flax produced in the Courtrai district, where the *running water steep* is largely practised. The flax is steeped in the slowly running waters of the river Lys; the straw is packed for the purpose in large crates, which are kept submerged by fastening them to stakes in the bed of the river. The duration of the steeping varies from 5 to 20 days according to the temperature. A necessary condition of preparation on this system is that the straw must be at least one year old, and it is often kept for two years before steeping. The steeping is frequently repeated.

The treatment practised in this country is that of steeping in stagnant water. A fermentation is set up, at the expense of the nitrogenous constituents of the stem, and of those non-nitrogenous bodies which are more easily attacked, with the result such as we have indicated. Such a process of spontaneous decomposition is necessarily difficult to control, and there have been many attempts both to regulate the fermentation by bringing the conditions under control, as well as to substitute for the fermentation other hydrolytic agencies or reagents.

The simplest of such artificial methods is that of Mr. Michael Andrews of Belfast, of which an account was given at the Flax Congress at Vienna 1873 (v. Exhibition Reports, Pt. 4, 656). This was founded on the well-grounded assumption 'that the most promising system would be to endeavour to imitate the best results attained by the ordinary method under the most favourable conditions,' these being secured by a definite temperature, uniformly maintained. The chief features of this artificial system consisted in steeping the straw in vats contained in a chamber, the temperature of which was controlled by means of steam pipes, the water being introduced at the required temperature (22-26°), and the heat kept up by the surrounding atmosphere of the chamber. In other words, the main purpose of the system was the creation

of an artificial climate. Under these circumstances the fermentation is in full vigour in 24 hours and continues uniformly for some days (6-10), when it gradually subsides as the operation approaches completion. The average loss of weight sustained by the straw is 23.7 p.c. and the average yield of fibre from the retted straw is 23.5. The scutched fibre yields on the average 75 p.c. of pure cellulose. The warm water retting process introduced by Schenk some forty years ago differed from the above only in the means employed to keep up the temperature of the vat, which was by the introduction of 'live' steam. Watts' process (1882) may be described as one of *maceration* or softening by the application of steam and water, without decomposition. The straw was placed in close chambers resting on a perforated bottom. The steam was driven in beneath, the condensed water being drawn off from time to time. The duration of the steaming was 10-12 hours. This process has failed to establish itself, as have also Schenk's and Andrews' (Irish Textile J. 1887-8).

A more radical departure in the treatment of flax is the process recently invented by M. Parsy, which will be found described in *L'Industrie Textile*, 1886, p. 511; 1887, p. 163. This consists in a treatment with water and steam at high temperatures, in a sealed apparatus (digester). The flax being suitably piled in the latter, water, or rather waste liquor from a preceding operation, is introduced at the boiling temperature; the valves being closed, the temperature is raised to 125°, and the solution allowed to remain half an hour in contact with the straw; it is then blown off, and steam is admitted under a pressure of 5 atmospheres, the steaming being continued for one hour. The steam is then blown off, the straw removed and artificially dried in a special apparatus. We have as yet no trustworthy reports as to the quality of the fibre yielded by this treatment.

There remain to be briefly noticed those processes in which the action of water at and above the boiling-point has been supplemented by chemical agents contained in solution.

J. R. Dry patented in 1876 (Eng. Pat. No. 4,721) a process of boiling in solutions of soap. The authors have investigated this process with the result of showing that such solutions have a specific action of the required character, not possessed by other alkaline solutions (*e.g.* sodium hydrate and carbonate) used in equivalent quantity and under the same conditions. But although the straw is effectually retted, the process is difficult to control, and the fibre, although of exceptionally good colour, appears to be lacking in spinning qualities. It appeared probable, however, that under investigation these defects might be overcome, in which case the only remaining point for consideration would be the important one of economy, upon which more than one of these artificial systems have broken down.

A process patented by one of the authors in 1880 (No. 4,984) has been worked with success upon the closely related fibre, hemp. In this case, however, it is not the raw material, but the scutched fibre which is treated. It consists in boiling under pressure (1 to 3 atmospheres) with a solution (1-2 p.c.) of sodium sulphite.

Under this treatment, a certain proportion of the fibre constituents are dissolved, with the result of a partial bleaching of the hemp, and the fibre bundles are partially disintegrated, so that the fibre can be spun to finer numbers of yarn, at the same time there is no deterioration of strength or spinning qualities. The process has also been tried experimentally on flax straw, and with favourable results, but not on a sufficient scale to enable a judgment to be formed as to the probability of its being industrially developed.

For the separation of hemp a preliminary retting is also necessary, but owing to the greater development of stem in this plant, the operation of separating the fibre is a purely mechanical one.

In the stem of the tropical jute plant the development of the bast is also of such a character that it is separable from the wood, after the steeping, by a simple manual operation, the stem, *i.e.* the wood, being broken across, the fibre and bark are stripped together, the latter being then broken away by striking and shaking on the surface of the water. The Rhea fibre is also freed with comparative ease from the wood, but the adhesion of the cortical tissues to the bast renders the isolation of the fibres a matter of some difficulty.

These illustrations are sufficient to indicate the general principles upon which the processes of isolating the dicotyledonous textile fibres depend.

Bast tissues of perennials, *e.g.* the *Adansonia*, are obtained by the simple process of stripping the growing tree.

The monocotyledonous textile fibres, *e.g.* Manila and Sisal, are separated from the fleshy leaves which yield them by means of a simple machine which crushes the soft parenchyma, the resulting pulp being then washed away from the fibre.

Next, and last in order, we have those fibrous substances from which no fibres can be satisfactorily isolated until after the material has been subjected to a chemical treatment more or less drastic according to the more or less resistant character of the substances with which the fibres are associated. These treatments we now proceed to describe.

(b) In this section we include the boiling or pulping processes of the papermaker. The raw materials for the paper-making industry are largely made up of the rejecta, of all kinds, of the textile arts, and the treatment of the waste products for the isolation of the materials differs in many cases only in detail from the bleaching processes auxiliary to those arts (*v.* article BLEACHING). These we leave out of consideration. Regarded from our chemical point of view we may divide papers into the two classes (1) those which are made up of a compound cellulose, usually a ligno-cellulose, *e.g.* cap and wrapping papers manufactured from jute (boiled or pulped with lime), *Adansonia* bast, mechanical wood-pulp, &c.; and (2) those composed of a pure cellulose obtained from a compound cellulose by completely eliminating its non-cellulose constituents. Of the former, papers made from jute pulp may be taken as representative. In this industry the more highly lignified root ends of the fibres or filaments are



employed. They are boiled with lime at a steam pressure of 10-20 lbs. This treatment has a very considerable softening and disintegrating action, removing or facilitating the removal in the subsequent treatments of the grosser impurities (admixtures of bark and cellular parenchyma, encrusting substances, &c.), and resolving the fibre bundles. At the same time the essential chemical characteristics of the fibre substances are not affected, and in the bleaching process (treatment with a solution of bleaching powder) which follows, it is only the more highly coloured products of the action of the base which are removed, the final product being a purified ligno-cellulose of a more or less deep yellow colour. And in like manner with all similar treatments of such compound celluloses. On the other hand a treatment with caustic solution at high temperatures effects a complete resolution into cellulose (insoluble) and non-cellulose (soluble derivatives), so far at least that the subsequent bleaching process, by oxidising and removing the residues of the non-cellulose which remain combined with the cellulose, brings the latter into such a condition of purity that it no longer gives the reactions characteristic of the non-cellulose in the raw material.

In addition to the process of digestion with caustic soda solution, we have other processes very different in character but effecting the same general result—viz. the isolation of cellulose, therefore also to be included in this second group of treatments; these are the various processes of digestion with acid reagents. The latter are, or have been applied to one class of raw materials only, viz. the woods; the alkaline processes on the other hand are applied to these as to all other fibrous substances. For the purpose of a general view we must consider them in relation to this one class of raw material, viz. the woods (fir and pine) to which they are each and all industrially applicable. The tabular view of these processes subjoined is based upon the principles enunciated in the earlier part of this article.

#### *Chemical Processes for Disintegrating Wood.*

(A) *Water* (150°).—Hydrolysis aided by acids formed from wood. Limit of action determined by reversal of hydrolysis, i.e. dehydration aided by oxidation.

(B) *Water together with neutral sulphites* (180°).—Simple hydrolysis. Products removed from sphere of action by combination with base and sulphite residue. Oxidation prevented by presence of sulphite.

(C) *Aqueous Alkalis. Caustic soda* (150-180°).—Hydrolysis aided directly by alkali, indirectly by combination with products of resolution.

(D) *Alkaline Sulphides* (150-180°). Hydrolysis aided by alkaline bases directly and indirectly by combination with products. Reversal of hydrolysis lessened by presence of reducing agent.

#### *Aqueous Acids.*

(1) *Oxidising and hydrolytic.*

{ Nitric acid (60-80°).

(E) { Hydrolysis aided by combination with nitrogen-oxides.

(2) *Simply hydrolytic.*

(F) { Hydrochloric acid (100°).

{ Limit determined by reversal.

(3) *Reducing and hydrolytic.*

(G) Sulphurous acid (80°-100°).

(H) *Bisulphites.* Hydrolysis aided primarily by sulphurous acid, also by combination of products with bisulphites and prevention of oxidation.

Of the processes enumerated above, only (C) and (H), and to a less extent (A) and (D), have attained to a position of any considerable industrial importance; we shall consider them, however, rather in regard to their chemical significance.

(A) The water process was studied by Fry and worked on an industrial scale (1866, *v. J. Soc. Arts*, 31, 223). The yield of brown pulp—disintegrated but unresolved ligno-cellulose—amounted under the most favourable conditions to about 70 p.c. of the original wood. The soluble non-volatile products were powerfully acid bodies playing no doubt a part in assisting the hydrolysis which, however, with the accumulation of aldehyde products and the increasing tendency to reversal of the hydrolysis with increase of temperature, rapidly attains a limit of conversion into soluble products represented as already indicated by about 30 p.c. of the wood substance.

(F) *Hydrochloric acid.* The action of this stable acid is one of simple hydrolysis, and resembles the one described above. A process founded on its action was worked by Baehet and Maehard for some time in Switzerland; the wood being boiled with the dilute acid, the resulting pulp made into a coarse packing paper, the solution being neutralised and subjected to an alcoholic fermentation.

(E) *Nitric acid.* With the oxidising acids, e.g., nitric acid, on the other hand, a very different result is obtained. The action of this acid on the ligno-celluloses, already described, p. 281, was applied by Coupier and Mellier (1852) and Barre and Blondell (1861) for the isolation of cellulose from wood. The process consisted in digestion with 50 p.c. nitric acid for 24 hours at 60-80°; washing the resulting pulp till free from the soluble products, boiling with a weak alkaline solution to remove residual nitro-products, and finally bleaching in the ordinary way. The yield of pulp would be about 40 p.c. As already stated, the action of this acid in presence of urea, is exactly that of the stable mineral acids. Under ordinary circumstances therefore this simple hydrolysis is reinforced by an oxidising action, attended by combination of the non-cellulose (derivatives) with the nitrogen oxides resulting from the reduction of the acid.

(G) *Sulphurous acid* in aqueous solution (minimum 7.5 p.c.  $\text{SO}_2$ ) effects a resolution which is especially remarkable from the fact that the soluble products differ in no essential characteristics from the non-cellulose as it exists in the wood. The names associated with the industrial development of this process are Tilghmann (1866) and Pietet (1882), the former, however, by the suggestion rather than the practical realisation. Pietet pulps the wood, by digestion in a sealed vessel, lead lined, at 80-100° and

under the corresponding pressure. After 16 hours' digestion the sulphurous acid is expelled by placing the digester in suitable connection with a second containing cold water or a more dilute acid requiring to be brought up to the requisite degree of concentration. In this way the sulphurous acid is very completely (90 p.c.) recovered. The wood is entirely disintegrated, 40 p.c. of its substance being converted into soluble modifications; the brownish pulp when bleached yields a pure cellulose, the proportion being 10-50 p.c. of the original wood. In regard to the mode of action of the sulphurous acid, there is no evidence of its undergoing any change, we must therefore account for the more complete hydrolysis, in comparison with sulphuric and hydrochloric acids, by its temporary combination with the products of hydrolysis under the special conditions of the digestion.

(II) *Bisulphites of calcium and magnesium.*

In this section we have a group of processes of growing importance, with the development of which a number of names are associated, *e.g.* Tilghmann (1856), Mitscherlich (1874), Ekman (1881), Francke (1881), Graham (1882), McDougall and Partington, Flodqvist, Kellner and others. The several systems developed by these inventors are identical in principle, though differing in such details as are in many cases of first importance technically considered. The solutions employed vary somewhat in regard to sulphurous acid strength (3-5 p.c.) and proportion of base, so also the temperatures and durations of the digestions necessary for complete resolution (150-170° and from 30 to 8 hours respectively). Special apparatus, *viz.* a lead-lined digester, is of course necessary. In the preparation of the bisulphite solution, the source of the acid is either sulphur or pyrites burnt in suitable ovens; the gas being either led into towers where it meets a constant, well-distributed supply of water flowing over and down the columns of basic material (calcined magnesia or lime), or a milky mixture of the latter with water; or lastly it may be led through vessels containing the milk of lime or magnesia kept in a state of agitation by special apparatus.

The pulp yielded by these processes is of a cream to brownish shade of colour, notwithstanding which, however, it takes a somewhat large proportion of bleaching powder (15-30 p.c.) to bring it to a good white (pure cellulose). The percentage yield varies from 40 to 50, the loss sustained in bleaching being small. The solutions from the digestion are of a bright yellow colour, and contain remarkably stable compounds of the aldehydic products of resolution, with the bisulphite molecule, together with a certain proportion of the non-cellulose in combination with the products of reduction of the sulphurous acid, *e.g.* mercaptans. It is the formation of the aldehyde-bisulphite compounds which plays the important secondary part in facilitating the hydrolysis of the ligno-cellulose, by preventing reverse actions at the high temperatures which are necessitated by the presence of the base, as well perhaps as the relatively small percentage of the acid.

(B) *Normal sulphites.*—The evidence we have as to the action of these compounds leads us to

assign to them only an indirect part in the hydrolysis; by combining with the products of the aqueous hydrolysis they prevent the reverse actions which would otherwise occur and so keep an open path for the continued action of the water at the high temperature. For the resolution of ligno-cellulose by means of solution with sodium sulphite (5 p.c.  $\text{Na}_2\text{SO}_3$ ) high temperatures (180°) are necessary. The process has this advantage that the digestion can be conducted in ordinary iron vessels, but there are disadvantages in point of economy which prevent its competing with the bisulphite or the alkali processes about to be described.

(C) In this group of processes the chemical agent employed is caustic soda. The strength of the solution, proportion of this to the fibrous material, the temperature and duration of the digestion vary considerably for the different classes of materials. Of these, in addition to wood, we may cite Esparto and straw, as being two of the most important of the staple raw materials of the paper manufacture of this country; the woods, on the other hand, are extensively employed in America and on the Continent. In the treatment of Esparto and straw the quantity of caustic soda employed varies from 10-20 p.c. of the weight of the raw material, the temperature of the digestion from 125° to 150°, and the duration from 8-12 hours. For the resolution of wood higher temperatures 150-180° are necessary. The chemical changes which take place are exceedingly complex, as is shown in the results of the investigation of the soluble by-products (*Papier Zeitung*, 1873, 226).

The action further differs from that of the sulphurous acid and bisulphite digestions, in being extended to a much greater extent to the cellulose itself. The evidence of this is in the lower yield of pulp. Thus the yield from white pine by the soda process is approximately 33 p.c., whereas by the bisulphite processes it is from 45-50 p.c.

The external characteristics and paper-making qualities of these pulps are also very different from those yielded by the bisulphite processes, the chief features of difference being their greater softness and opacity. The main point in the economy of this process is the recovery of the soda by evaporation and calcination, the organic matter dissolved supplying the fuel for this latter portion of the process. Indeed, with the present low cost of soda and the small cost of evaporation under the improved system of modern times, the process has to some extent revindicated itself over the bisulphite processes, which for some time threatened to displace it altogether. The struggle between these rival systems has, however, yet another phase before it. Hitherto the soluble by-products of the bisulphite processes have not found any industrial application, notwithstanding that they preserve intact the main chemical features of the non-cellulose of the original wood. When such an application has been worked out there must ensue another readjustment of the relative industrial developments of the two systems.

(D) A process based upon the hydrolysing activity of an alkaline mixture in which the sulphides preponderate is now worked with

success on the Continent. The starting point for the alkaline mixture is sodium sulphate. By treatment with lime a certain proportion is causticised. In this solution the wood is digested at the temperature of 150–180°. The solution from the boiling is afterwards evaporated, calcined, and treated with lime, by which treatment a solution is obtained containing sulphide and hydrate (together with sulphate) in nearly equal proportions. With the addition of sulphate to compensate for unavoidable loss, the cycle of operations is kept up. The final product is a pulp of very high quality, similar in all its characteristics to that yielded by the soda process. The only feature of difference indeed from the preceding group of processes is the presence of the sulphur, which complicates the action by the formation of organic sulphur compounds which it is scarcely necessary to add are very malodorous.

The processes above described yield pulps varying in degree of purity, *i.e.* percentage of cellulose, and necessarily also in quality. Those from the bisulphite processes yield harder and more transparent papers than those prepared by alkaline treatments. At the same time their colour is such that they may be employed directly, without further bleaching, for a very wide range of tinted and low white papers. For fully white papers they require, like the soda pulps, the ordinary process of bleaching, and consume from 15 to 25 p.c. of their weight of bleaching powder.

A process effecting both results *i.e.* hydrolysis and bleaching, in one operation, has been devised by C. Kellner (Engl. Patent 15,912, 1886). The principle of the process is a digestion of the wood with a solution of common salt at 125°, the salt solution being continuously electrolysed. From the liberated ions are produced on the one side caustic soda, on the other chlor-oxygen compounds of well known bleaching activity. Two digesters in communication are employed, and the liquid is kept in continuous circulation from the electrolysing vessel over the wood in the digesters and back to the electrolyser. The latter is a separate vessel in communication by means of pipes with both digesters. By this process, which need not be described in further detail, the inventor claims to produce a 'snow-white' cellulose at the one operation.

There also remain to be briefly noticed those systems of pulping lignified raw materials which employ chlorine gas as a disintegrating rather than as a bleaching agent. These depend upon the action of chlorination already described. They are, in fact, the carrying out on a commercial scale of the laboratory process of isolating cellulose. The process is chiefly applied to straw and flax (scutching waste). The material is partially resolved by alkaline treatment, washed and exposed for some hours to chlorine gas. The products of chlorination are removed by boiling in alkali. A slight subsequent treatment with bleaching powder completes the purification of the cellulose.

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C. F. C.

**CEMENTATION** *v.* IRON.

**CEMENT COPPER** *v.* COPPER.

**CEMENT STEEL** *v.* IRON.

**CEMENTS.** Under the comprehensive title of cements may be classed all substances capable of uniting two or more substances by adhesion to their surfaces, and by the cohesion of the particles of the cement.

The most important of these are used in the construction of houses, sewers, piers, bridges, lighthouses, docks, and harbour works. The subject may, therefore, be divided into

I. BUILDING CEMENTS.

II. RESINOUS CEMENTS AND ADHESIVE MATERIALS.

Under the head of BUILDING CEMENTS, the following subjects are treated:—

1. LIME-BURNING.

2. MORTAR.

3. PLASTER OF PARIS.

4. HYDRAULIC MORTAR.

5. POZZUOLANA.

6. HYDRAULIC CEMENT.

7. ONYCHLORIDE CEMENTS.

8. ARTIFICIAL STONE.

9. CONCRETE.

1. **Lime-Burning.** To obtain lime,  $\text{CaO}$ , it is necessary to decompose the carbonate  $\text{CaCO}_3$  by heat. The process is called lime-burning and the product lime or *quick-lime*.

The decomposition begins at about 300°C., and the temperature which is usually employed is indicated by a bright red heat. It ought not to exceed 1100°C. The facility with which lime is burnt depends upon the porosity of the limestone and the size of the lumps. Furthermore the expulsion of carbon dioxide is facilitated by the introduction of steam into the mass, a fact which was first demonstrated by Gay-Lussac, and which is known to practical lime-burners, who water limestone if by prolonged standing in the open air it becomes dry.

The passage of a large volume of air through the heated limestone also favours the disengagement of carbon dioxide. The reason of this is the peculiarity of the decomposition, which is dependent upon the temperature of the limestone, and upon the tension of the carbon dioxide in the atmosphere surrounding the limestone. Such conditions of decomposition are characteristic of the phenomenon called *dissociation*.

Dorlhac and Saminn have shown that the same lime when simultaneously burnt in air and in a current of steam loses 3.1 p.c. more  $\text{CO}_2$  in the steam than in the air. They also proved that lime increases in volume when burnt. A cylinder 27 mm. long and 17 mm. thick became after burning 28 mm. and 17.7 mm.



According to the nature of the limestone the lime will turn out to be —(a) a 'fat' lime, (b) a 'poor' lime, or (c) a hydraulic lime.

If it contains more than 10 p.c. of silica, a lime must be classed as hydraulic, because the paste which such a lime forms when slaked with water will set in water, or in moist places where it is not exposed to the drying influence of the air.

The process of lime-burning may be carried on in four different ways.

1. *Intermittent burning with a long flame.*
2.   "               "               "       *short flame.*
3. *Continuous burning with a short flame.*
4.   "               "               "       *long flame.*

#### LIME-KILNS.

*Intermittent burning with a long flame.*—For calcination with a long flame, and intermittently, the primitive form of kiln fig. 1 is constructed by making a circular hole A in

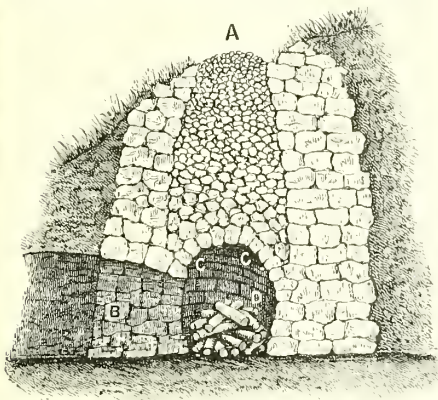


FIG. 1.

the side of a hill, or on a slope; the interior is lined with large stones of the same material as those to be burnt. At the bottom of the kiln there is a horizontal passage to the outside. The end of the passage B in the interior of the kiln is arched over C, and a fire of wood, or peat, D is lighted as soon as the kiln has been charged. The charging of the kiln is so carried out that the bottom contains the largest lumps of limestone, and the top the smallest pieces.

A kiln so simple will, as a matter of course, use more fuel than is absolutely necessary.

Fink's kiln fig. 2 has an internal form which is ovoid (B); between the inner layer of refractory brick which lines the furnace and the outer wall, there is placed a packing of sand (E) or ashes, which prevents damage to the outer wall and loss of heat. The hearth of the kiln fig. 3 is formed of five arches of refractory brick F, with a space between them of 6 inches; upon these are placed rows of bricks, transverse in direction, and of material equally refractory; the spaces which are left allow of the passage of the gases from the furnace. The bottom of the kiln has two oppositely situated openings which lead to the passages where the lime is withdrawn (C); below these are two hearths (AA) with gratings

and ash-pits. The mouth of the kiln can be closed hermetically at the end of the operation by means of an iron cover (D) upon which is a thick layer of sand retained by a rim. The

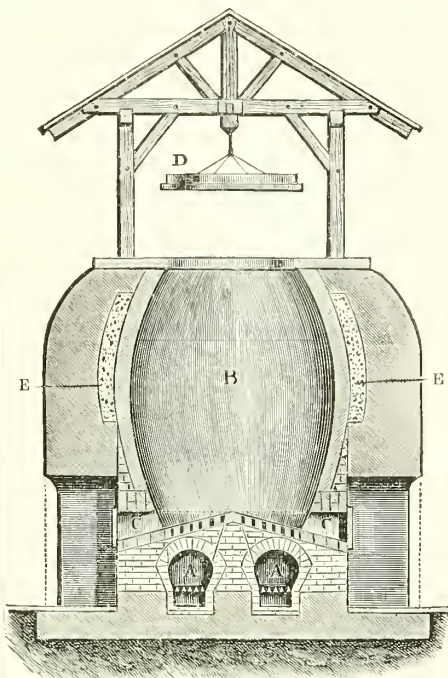


FIG. 2.

cover is suspended from a cross beam, supporting a roof which covers the upper platform of the kiln, and prevents the rain or snow from

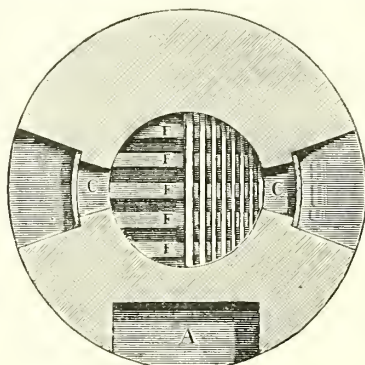


FIG. 3.

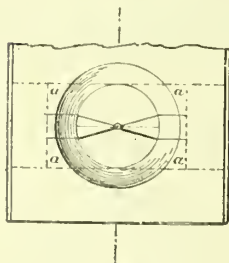
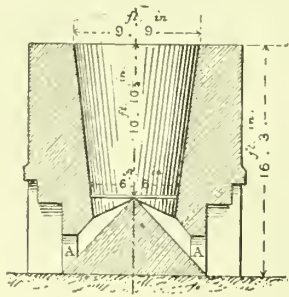
lodging on and cooling the kiln, which would be injurious to the progress of the burning.

The cover may be raised or lowered at will by a pulley. The fuel used is the most combustible kind of wood. This furnace is very much used in certain industries.

*Intermittent burning with a short flame.*—In this mode of lime-burning the fuel and lime-

stone are arranged in alternate layers. Turf and coal are much used for the purpose. Attention must be paid to the packing of the kiln so as to admit of a free passage of air through every part. The interior of the kiln narrows towards the bottom. A charge is burnt in three or four days. When cool it is removed from the furnace in such a manner as to keep the ashes of the fuel from the lime. The charge contracts very greatly as the fuel burns away, hence the gradually diminishing capacity of the kiln towards the bottom. Lime should not be burnt in this manner except for agricultural purposes, since the ashes of the fuel impair the quality of the lime.

*Continuous burning with a short flame.*—The mixture of alternate layers of limestone and fuel is more frequently applied to the continuous



Figs. 4 and 5.

than to the intermittent system of lime-burning. The proportion of fuel to limestone in a charge varies with the nature of the fuel and the size of the pieces of stone, but the average is 4 parts of stone to 1 of fuel. Coke is to be preferred to coal, being free from bituminous matter and capable of furnishing a white and purer product. The rational shape of a kiln is internally that of a reversed truncated cone, or at any rate some form which diminishes regularly, the mouth being of greatest, and the hearth of smallest diameter. At the lowest part of the furnace there is ample provision for removing the burnt lime.

Figs. 4 and 5 represent a vertical and horizontal section of a kiln used in France on the Paris and Lyons railway. The burnt lime is withdrawn by four openings (a) placed at the opposite sides of the kiln. Two such kilns, with a total capacity of 34 cubic metres, or 1,200 cubic feet, furnish on an average 10 cubic metres of lime per day or 275 bushels.

A much more perfect form of kiln is that of MM. Pavin de Lafarge (fig. 6). The interior is like a hollow spindle, the mouth is provided with a cover which prevents loss of heat, and the interference of the draught by gusts of wind is prevented by a flue near the

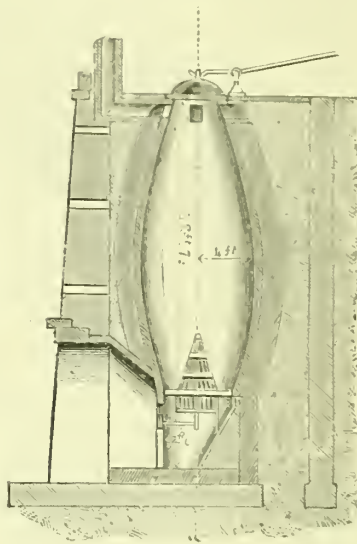


FIG. 6.

mouth, in which a valve serves to regulate the draught and maintain a constant temperature. The bottom of the kiln is barred by a grating fixed conically so as to direct the pieces of lime and thus facilitate their withdrawal. The opening to the furnace is provided with a cast-iron door, which is closed when work is temporarily suspended.

The average quantity of coal burnt is 2 to 4 loads for every 10 of burnt lime. A load of turf yields an equal measure of lime.

*Continuous burning with a long flame.*—There are several forms of kiln for carrying out this method; the supply from them is constant, and may be large in amount, and the consumption

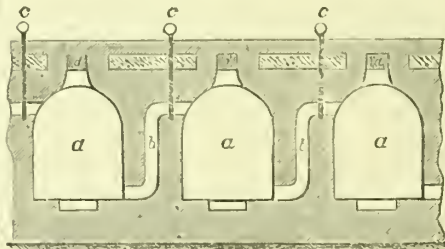


FIG. 7.

of fuel in the best of them is reduced to a minimum, while an inferior quality of fuel may be used.

In Swann's kiln fig. 7 two rows of several connected chambers, a, are so arranged that the heat from a fire passes from the bottom of the

first chamber to the top of the next. The passages (*b*) can be closed or partly opened by valves (*c*) placed in them, which are manipulated from outside. The fuel is not mixed with the limestone, but burnt on a movable hearth kept in constant motion, and self-feeding.

The greatest improvement in lime-burning consists in the application of the Siemens' gas-producer to the heating of limekilns. F. Steinmann was the first who succeeded in this direction.

Figs. 8 and 9 represent a vertical section

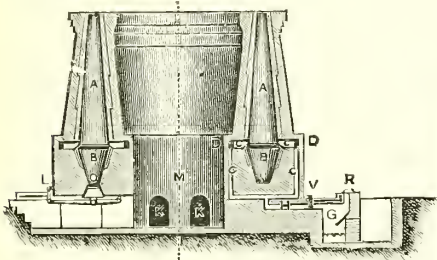


FIG. 8.

and plan of his kiln. AA is the kiln, which is of an annular form; BB is a receptacle for the burnt lime; G is the gas producer; H, the passage for the gas; c branches off the main passage; D, circular conduits by which the gas is distributed round the periphery of the kiln after passing through c; O is an opening for

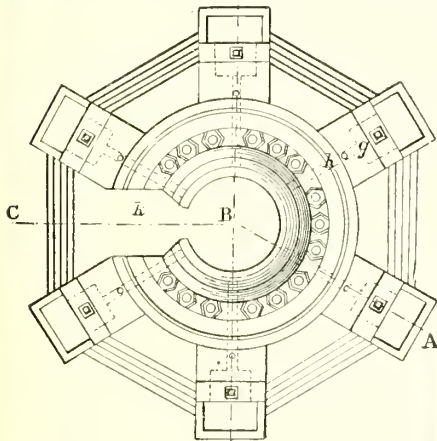


FIG. 9.

withdrawing the lime after it has been burnt. It has a fitting of cast-iron and a conical stopper of fire-clay, which is moved by a lever L, which regulates the necessary admission of air for burning the gas. Air admitted by this opening is heated by contact with burnt lime, which mixes with the gas in the conduits and causes its combustion. The six doors K admit to the central space where the limestone to be used is previously stored.

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Before filling the kiln every part must be dried, otherwise it would be impossible to light the gas. After the preliminary drying the bottom of the store for lime is covered with easily combustible wood, and spread over this is a layer of charcoal or turf 1 foot to 18 inches thick, after which alternate layers of limestone and charcoal are piled up to 20 inches above where the gas enters. From this point upwards the space is filled with limestone. Gas is next prepared in the producer by lighting shavings and brushwood upon the bars, after which the grate is filled with fuel. When the flames reach the openings c, the gas is lighted. The first quantity of lime is

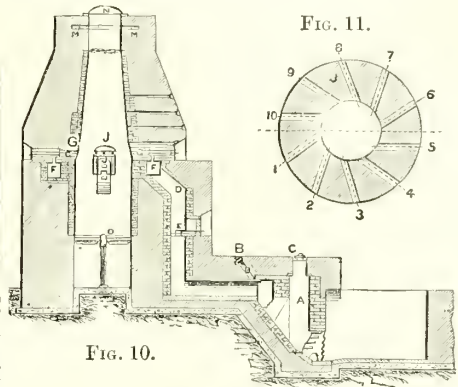


FIG. 10.

removed at latest 3 hours after the introduction of gas from the producer. Subsequent quantities are drawn at intervals of 1, 1½, and 3 hours. After each removal the kiln is again filled up. Before feeding the producer with fuel the valve at v is closed to prevent an explosion by opening the stokehole R.

A kiln heated by a gas-producer, designed

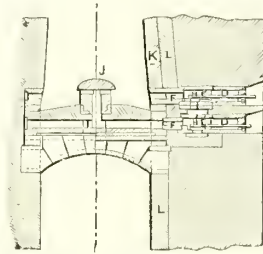


FIG. 12.

by Vigreux and Leroy-Desclosages, and built at Champigny, is somewhat different in detail. It is represented in the figures 10, 11, and 12. The body of the kiln is shaped like a cylinder, surmounted by a truncated cone (fig. 10). Its interior lining K, fig. 12, consists of blocks of compact limestone, which resist the action of heat, and of caustic lime. The bottom of the kiln is closed by a double grating O, fig. 10, access to which is obtained from the passage where the lime is removed. The upper part is covered, N, and a flue M allows the escape of gas. The gas-pro-

II H



ducer is far enough removed to admit of the cooling of the burnt lime. *c* is the stokehole, and *b* an opening to the hearth. The gas is led by *d* into a circular flue *f*, and being distributed among the different burners *a* regularly spaced in the perimeter of the kiln, feeds in addition a central hearth *j*, shaped like a mushroom and pierced laterally with openings which correspond with those of the burners. (See horizontal and vertical sections in figs. 11 and 12.) The central hearth is supported by an arch of refractory brick, which rests against the walls of the kiln. A valve *e*, placed in the main flue *p*, and other valves *u* corresponding with each burner, serve to regulate the combustion of the gas. An intense and very regular heat may be obtained by this arrangement.

The kiln at Champigny has a capacity of 10 cubic metres or 353 cubic feet, and it produces 6 cubic metres of lime in the 24 hours, equal to 165 bushels.

There is an average consumption of 4 cwt. 20 lbs. of coke for each ton of quicklime (Génie Civil, July, 1882).

**2. Mortar.** By the term mortar is usually implied a mixture of lime and sand, which dries when exposed to the atmosphere. It is employed in the cementing of brickwork and masonry, also for covering the external walls of buildings. When mixed for use it should be of the consistency of a soft paste which will fill the interstices between building materials. It should adhere, and in course of time become as hard as stone. The durability and strength of mortar depends upon the nature of the lime and of the sand employed in the mixture. Thus in the mixing of mortar quicklime is slaked with water, and in the consistency of cream is mixed with sand, the latter substance being added to prevent the mass shrinking as it dries. If the limestone consists chiefly of pure carbonate of lime, then the lime obtained therefrom is termed a 'fat' lime; on the other hand, if the limestone contains magnesia, it forms a thin, poor mixture with water, and is termed a 'poor' lime. With 10 p.c. of magnesia a lime is 'poor,' and with 25 to 30 p.c. is almost useless. The occurrence of considerable quantities of magnesia in limestone prevents it from being satisfactorily burnt, and accordingly it does not slake properly. The best lime combines with about one-third of its volume of water, and evolves a large amount of heat, while it combines with the water to form calcium hydrate. The temperature may rise as high as 150°C., and it is always sufficient to drive off a considerable quantity of water as steam. During slaking it largely increases in bulk, and the hard mass of burnt lime falls to powder. Should the limestone contain a certain proportion of silica and alumina, these substances, when the lime is being burnt in a limekiln, are likely to combine with some of the lime to form a slag, and fuse or form a hard crust upon the surface of the lump. This covering then protects the quicklime beneath the surface from being acted upon by water.

Lime cream alone might be used as a cement, but on account of the shrinkage which would take place its use would be attended with difficulty. This shrinking is observed when slaked

lime is simply exposed to the air; it is always accompanied by the absorption of carbonic acid and the formation of a calcium carbonate. Certain limestones which contain more than 10 p.c. of silica possess the property, when burnt, of making a mortar which will harden under water. The lime obtained from such limestone is termed *hydraulic lime*, and mortar prepared therefrom is known as *hydraulic mortar*.

#### VARIETIES OF SAND.

The nature of the sand to be used for making mortar is of some consequence. Sand consists of the small particles of disintegrated silicious rocks, and the composition of these particles is therefore much the same as that of the rocks from which they are derived. Angular or 'sharp' sand is to be preferred to that which consists of smooth round particles like sea-sand, for the varieties resembling this latter always yield a brittle mortar. Again, the size of the particles is of much consequence. With sand there is sometimes much dust, but dust and sand may be separated by washing; particles so fine that they render water turbid cannot be considered as sand, for sand immediately sinks to the bottom of the water, and, if clean, does not interfere with the transparency of the water.

Sand properly so-called may be distinguished as *coarse sand* and *fine sand*. The former consists of particles varying in size from the  $\frac{1}{32}$ th to  $\frac{1}{8}$ th of an inch in diameter, fine sand from  $\frac{1}{16}$ th to  $\frac{1}{32}$ th of an inch. Sand should be free from clay, since this latter does not adhere to lime. Coarse sand is best suited for 'fat' limes; on the contrary, the finer kinds of sand are to be preferred for use with hydraulic lime (p. 464).

According to its mode of occurrence sand suitable for making mortar may be described as being of three distinct kinds, namely, *virgin sand*, or such as is obtained from rocks actually undergoing disintegration; *fossil sand*, or such as at some previous geological period has been deposited by water; and, thirdly, *river sand*, which is in course of transmission from its original source to the sea. The first not having been acted upon by water is frequently contaminated with clay; the second is a 'sharp' sand, which, when free from clay, is much desired for building purposes; the third is generally clean, but the particles are smooth and rounded by the continual motion communicated by the running water.

*Sea sand* is disadvantageous on account of the deliquescent salts, calcium and magnesium chlorides, which accompany it, and which retain or attract moisture to walls in which it is used; nevertheless it may be employed after thorough washing in running fresh water or after exposure to rain for some months.

#### THE SLAKING OF LIME.

The slaking of lime may be so conducted as to produce a paste or to obtain a dry hydrate. To obtain a paste, lumps of lime are placed in a pool of water 12 to 18 inches deep, much of the water is soaked up by the lumps which are not immersed completely; soon the masses begin to move and with noise to split, at the same time a small quantity of steam rises,

which increases until the whole crumbles to powder. At the close of twenty-four hours hydration is complete, and a homogeneous paste is obtained fit to be mixed with sand.

*To obtain a dry hydrate.* The lime may be slaked to powder in three different ways:

1. By immersion or soaking in water and removal therefrom.

2. By sprinkling with water.

3. By spontaneous hydration caused by atmospheric moisture.

1. Lime, in pieces the size of an egg, is placed in a basket of wickerwork or hoop iron, and is immersed in water for one or two minutes until hydration has well commenced, when it is withdrawn. The combination of water with the lime continues until the mass falls to powder, expelling a good deal of steam. Before the lime falls to pieces it should be quickly heaped together, or emptied into casks or bins and covered up, in order to concentrate the heat and prevent the escape of vapour. It swells, cracks, and becomes reduced to a fine powder. It is obvious that this method must be carefully carried out if a dry powder is to be obtained.

2. If lumps of lime placed in heaps are watered at intervals, so that the mass is equally moistened all through, the slaking proceeds as in the previous case, but with greater regularity.

3. If lime in pieces of the size of an egg is exposed to the air for not less than three months it will fall into powder consisting of a calcium hydrated subcarbonate. The water contained therein amounts to from 10 to 11 p.c. This means of slaking is applicable only to 'fat' limes.

The increase of volume of lime during slaking is considerable, as shown by the following statement, which applies to 'fat' limes only.

*100 volumes of quicklime yield of slaked lime.*

	'Fat' lime	Hydraulic lime
By slaking to paste,	250 to 300,	140 to 175 vols.
" to powder,	230,	130 to 150 "
" spontaneously,	260,	112 to 140 "

It is of considerable importance that the water used for slaking lime and mixing mortar be free from saline matter. River water is to be preferred. Water containing calcium sulphate in solution is injurious to the quality of mortar and retards its setting. Sea water, which of course is strongly charged with chlorides, with calcium and magnesium sulphates, is stated by Chatoney to retard the setting of the mortar. According to F  burier, sea water does not affect the hardening of mortar. There can, however, be no doubt that its use is undesirable for dwelling-houses, since the salts which remain in the mortar are deliquescent; they attract moisture, cover the joints between brick and plaster on walls with an efflorescence, and render dwellings unhealthy. On the other hand, for hydraulic mortars, sea water was used by Smeaton for the old Eddystone lighthouse and for many works afterwards, in preference to fresh water. It has been employed upon important works at Flushing, and also by General Michaud in the Isle of Elba, in each case with advantageous results.

*MORTAR OF THE ANCIENTS.*

The earliest examples of the employment of mortar in masonry are presented by the pyramids of Egypt. An examination of the mortar lying between the stones of the pyramid of Cheops has shown it to be identical with that in use in Europe at the present day, although its preparation must have taken place more than two thousand years before the Christian era (Vicat, *Traite th  orique et pratique de la composition des mortiers et ciments*).

Several analyses of ancient mortars have been made by Wallace, and the facts to be deduced from the results are interesting and important. The figures are given in the following table.

It will be observed that the carbonic acid estimated in the first six mortars corresponds with the amount necessary for the complete neutralisation of the lime and magnesia. In

*Analyses of Ancient Mortars (W. Wallace).*

Origin of the mortar	Silica and fine sand	Alumina $Al_2O_3$	Lime CaO	Coarse sand	Small stones	Ferric oxide $Fe_2O_3$	Magnesia MgO	Sulphuric acid $SO_3$	Carbonic acid $CO_2$	Potash $K_2O$	Soda $Na_2O$	Organic matter	Water $H_2O$	Total
1. <i>Phœnician Mortars.</i> Ruins of a temple at Larnaca, Cyprus	16.20	2.16	26.40	3.37	28.03	0.99	0.97	0.21	20.23	—	—	0.56	0.54	100.23
Mortar forming the joints of a buried watercourse at Larnaca	0.96	0.40	51.58	—	—	—	0.70	0.82	40.60	—	—	0.24	3.09	98.39
2. <i>Greek Mortars.</i> Mortar exposed to the air, taken from the Pnyx, Athens	12.06	2.64	45.70	—	—	0.92	1.0	—	37.0	—	—	—	0.36	99.68
From the interior of a temple at Athens	3.00	0.98	49.65	—	—	0.82	1.09	1.04	38.33	—	—	—	3.07	98.88
3. <i>Roman Mortars.</i> Villa Adrian, Tivoli	41.10	14.70	15.50	—	—	4.92	0.30	—	11.80	1.01	2.12	2.28	5.20	98.73
Wall plaster at Herculaneum exposed to the action of warm water	33.36	2.86	20.88	—	—	2.32	0.25	—	23.80	3.40	3.49	1.50	1.0	101.86
Roof of the Latin tombs, Rome	36.26	16.39	19.71	—	—	1.23	0.71	—	13.61	Not estimated	—	—	8.20	—
Mosaic on the floor of the Bath of Caracalla, Rome	30.24	10.64	25.19	—	—	3.67	0.90	—	17.97	—	—	2.48	5.50	—

the two last specimens only is the quantity of carbonic acid insufficient to carbonate the whole of the lime and magnesia. Either some of the lime has remained caustic or part of the lime has entered into combination with the aluminium silicate.

#### THE CAUSE OF THE SETTING AND HARDENING OF MORTAR.

When exposed to the air mortar sets some days after use. It can then resist the pressure of the fingers. The hardening follows the setting, but takes place much more slowly. It has been found in some cases after the lapse of centuries that mortar has not completely hardened. The cause of the setting of mortar is a process of drying by exposure to the air; on the other hand, hardening is due to an absorption of carbonic acid, which converts the calcium hydrate into calcium carbonate. Wet mortar does not absorb carbonic acid readily, it is only after it has set, that is, dried, that carbonation ensues. The process commences at the surface and passes to the interior of the mass.

If some fresh mortar be placed in a glass tube and carbonic acid be passed in for several days, it will be found that very little has been absorbed; the mortar has retained its condition of a wet paste. If plates of the same mortar be exposed to the air during the same time they harden and absorb a much greater proportion of carbonic acid.

Plates of fresh mortar suspended in an atmosphere of carbonic acid are found after eight days to be as soft as at first, and to have absorbed less than 1 p.c. of their weight of carbonic acid. But if they be placed in a vessel containing a jar of sulphuric acid so as to hasten the drying of the mortar, it is found that they gain as much as 11 p.c. of carbonic acid in a single day. Mortar behaves in a similar manner if moistened with a solution of ammonium carbonate. When fresh it does not harden, neither does it absorb carbonic acid; but after it has once set it becomes very hard, and the absorption of carbonic acid is very considerable.

On the other hand, mortar which is dried artificially as completely as possible, yields a compact mass which is very friable, and which neither absorbs carbonic acid nor hardens. It follows from these facts that the hardening of mortar is intimately connected with the presence of moisture.

A slow drying, after setting, favours the conversion of calcium hydrate into calcium carbonate; then during the hardening the particles which are first solidified soak up a solution of calcium hydrate which, by gradual evaporation, deposits the lime which it contains, and this binds the former particles together with a solidity which increases with the slowness of the deposit. The gradual deposition of calcium hydrate is favourable to its being acted upon by carbonic acid and its conversion into calcium carbonate. It will thus be perceived that the process is somewhat similar to the action of petrifying waters in which calcium carbonate is dissolved by carbonic acid, and, as this escapes, a hard coherent crust of calcium carbonate is deposited.

The admixture of sand is not an essential condition of hardening, though it greatly facilitates it by rendering the mass more porous and more easily accessible to the carbonic acid in the air.

Although lime generally appears to be without chemical action upon sand, nevertheless Petzholdt has found 2.1 p.c. of combined silica in a mortar one hundred years old, and 6.2 p.c. in mortar three hundred years old, while the lime used for the mortar contained no more than 0.11 p.c.

Petzholdt, by taking a pure lime burnt from Carrara marble, mixed with (a) artificial silica previously ignited, with (b) powdered quartz well washed, and with (c) white sand, showed that silica entered into combination with the lime. Thus:—

Composition of mortar	Percentage of soluble silica.	
	After 1 week	After 5 weeks
Mixture of 'fat' lime and calcined silica (a) . . .	0.59	4.10
Mixture of 'fat' lime and powdered quartz (b) . . .	0.04	0.60
Mixture of 'fat' lime and white sand (c) . . .	0.06	0.66

Rault has shown that the basic carbonates of lime have the property of hardening with water. If, then, we have a deposition of calcium hydrate upon the particles of sand in mortar taking place by evaporation, we may have the formation from this of a basic carbonate which will harden with the water set at liberty during carbonation. Thus it will be seen that the hardness of mortar which is not completely carbonated may be accounted for. The researches of Brigadier-General Q. A. Gilmore, A.M., of the United States, confirm the conclusion arrived at by G. Robertson—*The depth to which carbonic acid is absorbed into mortar in a given time, and, to a certain extent, the induration from that cause, varies inversely with the hydraulic properties of the lime, which depend upon the silica contained in it.*

**3. Plaster of Paris.** Plaster of Paris is gypsum partially deprived of water by heat. When again mixed with water it slakes and evolves a considerable amount of heat; at the same time it increases in bulk and eventually forms a hard mass, which is more or less dry but is always porous. According to Claudel and Laroque a cubic metre of plaster in powder becomes 1.18 m. when it sets. The facility with which it sets, its whiteness, hardness, and porosity make it applicable to a number of useful purposes. It was used to some extent for building purposes by the ancient Egyptians, as is evident from the analyses of Dr. W. Wallace of a specimen of plaster from the pyramid of Cheops.

#### Analyses of Plaster from the Pyramid of Cheops.

	No. 10. From the interior.	No. 11. From the exterior.
Hydrated calcium sulphate . . .	81.50	82.89
Silicic acid . . . . .	5.30	4.30
Calcium carbonate . . . . .	9.47	9.80
Alumina . . . . .	2.41	3.00
Ferrie oxide . . . . .	0.25	0.21
Magnesium carbonate . . . . .	0.59	0.79
Total . . . . .	99.52	100.99



It is largely used in Paris for building purposes and for the execution of decorative plaster work, for taking casts of statuary, of the human figure before and after death, for making moulds for pottery, and making rigid surgical bandages. When mixed, or 'tempered' as it is termed, for use with a trowel, much less water is required than when it is employed in a fluid state for taking casts. The trowels used are of copper, for iron is very readily corroded by plaster, and, moreover, the material adheres very persistently to the metal. In order to temper plaster for taking a cast, the powder is sprinkled little by little upon the surface of a considerable quantity of water; it soon becomes thoroughly wetted and sinks to the bottom. No more is added until the first layer has sunk. When the whole of the powder has been thus moistened, the milky liquid is poured off from the pappy material below, and this is poured into the mould. By proceeding thus, a small quantity is lost, but the plaster is of uniform consistency and free from air-bubbles, so that the cast is thoroughly sound.

#### THE BURNING OF PLASTER OF PARIS.

*Historical notes.*—The phenomena attendant upon the baking and hardening of plaster of Paris were first studied by Lavoisier, who was no more than twenty-one years of age when his first very remarkable memoir on the subject was published. In the *Comptes Rendus* of February 17, 1765, there appears a short note containing a passage of which the following is a translation: 'After having removed the water of hydration from gypsum by heat, if it be presented to it again (this is commonly known as the mixing or tempering of plaster), it takes it back with avidity, it suddenly assumes a state of irregular crystallisation, and the small crystals which form become confused with each other, the result being a very hard mass.' Lavoisier discovered that baking at too high a temperature removed from plaster its peculiar property of setting from a consistency of cream to a hard mass, and he signalled an important detail in the baking of plaster which has escaped authors who have since written on the subject. Water is removed from gypsum at two stages; the first three quarters of combined water are much more easily removed than the remainder. According to Zeidler gypsum or plaster commonly employed in stucco work is not anhydrous, but contains 5.27 p.c. of water; Berthier stated it to be from 4 to 8 p.c. and Landrin by recent researches has confirmed these statements. About 1830 Payen found that when heated in air, plaster began to lose water at 115°C. and its loss increased more and more rapidly as the temperature rose. If heated above 201°C. gypsum becomes 'over-burnt' and loses its value as plaster, since it refuses to set when mixed with water.

Gypsum or natural hydrated calcium sulphate is burnt for the purpose of removing only so much of the water as will yield a plaster capable of readily combining with water again when mixed therewith.

The mode of its preparation affects in a great measure the qualities of the plaster; the choice of the stone is of importance, the heavier and denser varieties yielding the best material.

Small quantities of gypsum may be burnt to plaster by heating in an iron pot over a fire until water no longer condenses on a cold plate held over the pot.

In large quantities gypsum is burnt in an oven or kiln, the precaution being taken that the fuel shall not come into contact with the calcium sulphate in such a manner as to cause

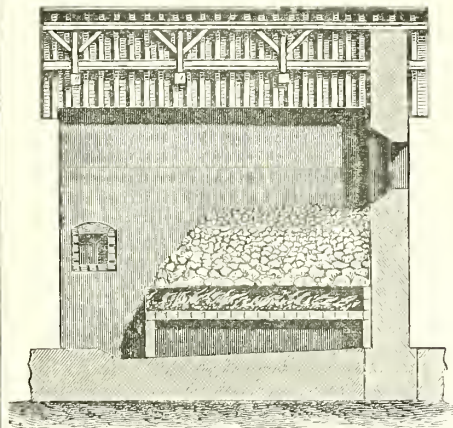


FIG. 13.

its reduction to sulphide according to the equation  $\text{CaSO}_4 + 4\text{C} = \text{CaS} + 4\text{CO}$ .

Of gypsum kilns the simplest form, most usually employed, consists of a chamber built of strong masonry, the roof being a flat arch with openings for the escape of steam and products of combustion. Fires of brushwood are lighted

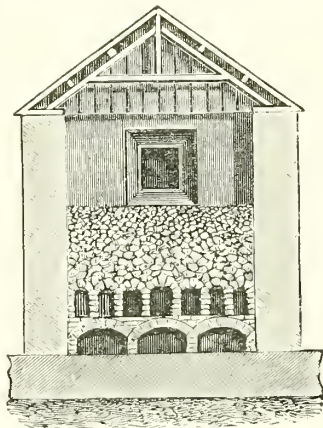


FIG. 14.

in a series of small arched fire-places, the arches being 3 feet above the floor. The gypsum, broken into lumps about the size of an egg, is piled above these arches half way towards the roof. The whole structure is covered by a tiled shed. See figs. 13 and 14.

The equal heating of all parts of the material is a point to be carefully attended to. The form of kiln used at Montmartre for burning

Paris gypsum is shown in fig. 15. *E* is the fire-place with an open arch of refractory fire-brick, *L* is the door for drawing the charge.

Seaneagatty's kiln is of improved construction. A domed chamber is divided unequally by an arch springing from about a foot above the floor. The gypsum is placed in the upper part

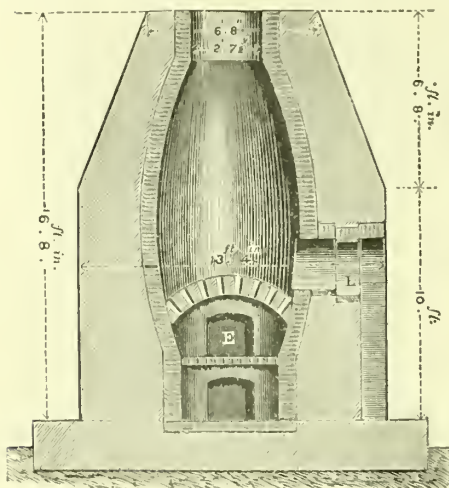


FIG. 15.

of the chamber. The space beneath the arch is in connection with the flue of a furnace, the flames from which are driven by the draught on to the under surface of the arch, through openings in which the hot air and products of combustion pass into the upper half of the chamber

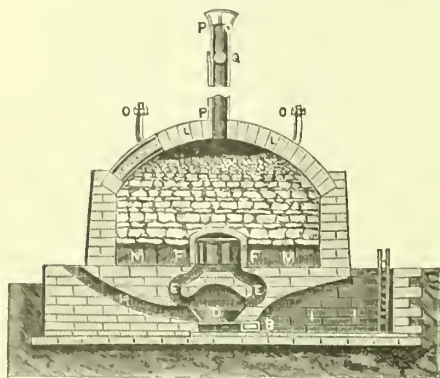


FIG. 16.

charged with gypsum, and finally escape from openings in the top of the dome. See figs. 16 and 17.

*The chemistry of the process.*—Payen by experimenting upon large quantities of gypsum made the following observations:—

1. The lowest temperature at which gypsum can be burnt is 80° C. and a long time is required to obtain plaster therefrom under this condition.

2. A temperature of 110° to 120° C. yields the best preparation for technical purposes.

3. In order that gypsum may be burnt equally all through it should be reduced to powder or be broken into small pieces.

M. le Chatelier, in a work published in 1887, quotes Payen's statement of the most suitable temperature, and points out that different authors have not been in accord in their recommendations, which embrace temperatures varying from 110° to 300° C.

To investigate the matter thoroughly he heated small quantities of gypsum in tubes placed in a paraffin bath heated gradually and progressively. A thermometer placed in the

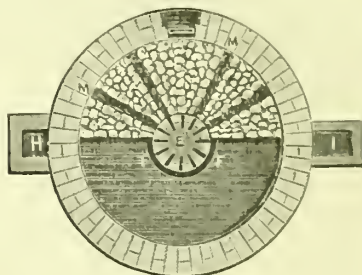


FIG. 17.

powdered gypsum marked its temperature and each successive rise of the mercury on the scale was registered by a chronograph. When a process of dehydration took place the mercury halted owing to the absorption of heat due to chemical change. In a rise from 100° to 200° the mercury halted for two intervals. The first halt occurred at a temperature of 128°, the second at 163° C. While absorption of heat during the former interval is undoubtedly due to dehydration, the second might be caused by a purely physical change in an anhydrous compound. The temperature showed that these changes were unequally marked in degree; hence it became necessary to settle the question by determining the loss of weight at or about the two temperatures.

The result proved that dehydration is incomplete at 155°, and that it is complete at 194° C. The quantity of water contained in pure gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is 21.4 p.e. The two periods when a halt is made in the temperature curve correspond to two distinct phases of hydration. The quantity of water lost during the first phase is perfectly definite, and corresponds to the formation of a hydrate with the composition denoted by  $(\text{CaSO}_4)_x \cdot \text{H}_2\text{O}$ . It contains 6.2 p.e. of water. The halting point marks the passage to the higher range of temperature notified by Lavoisier as necessary for the expulsion of the last fourth of the water of hydration. The proportions of water found by Landrin and by Zeidler in good plaster—namely, 7 and 5.27 p.e. respectively, differ but little from the theoretical quantity, which is 6.2 p.e. It now became necessary to determine whether plaster is a chemical compound or a mixture of anhydrous calcium sulphate with the sulphate containing two molecules of water.

A saturated solution of calcium sulphate, if heated in a sealed tube to a temperature lying between  $130^{\circ}$  and  $150^{\circ}\text{C}$ ., yields extremely delicate long rectangular prisms.

By taking an excess of gypsum mixed with water a larger yield of these crystals is obtained. The tube was broken while yet warm, the water for the most part evaporated, and the crystals were thrown into alcohol to prevent their combination with more water. The analysis of these crystals yielded—

*Composition of Plaster of Paris.*

	Found	Calculated for $(\text{CaSO}_4)_x \cdot \text{H}_2\text{O}$
Water	6.7	6.2 per cent.
$\text{CaSO}_4$	93.3	93.8 "
	100.0	100.0

The compound, therefore, possesses the composition  $(\text{CaSO}_4)_x \cdot \text{H}_2\text{O}$ .

The same hydrate is found in boilers fed with sea water, as shown by the following figures :

*Analysis of a Boiler Incrustation from a Transatlantic steamer.*

	Per cent.
$\text{CaOCO}_3$	0.3
$\text{Fe}_2\text{O}_3$	2.0
$\text{H}_2\text{O}$	5.8
$\text{CaSO}_4$	91.9
	100.0

The temperature at which this compound is completely dehydrated lies between  $160^{\circ}$  and  $170^{\circ}\text{C}$ . Broken up and mixed with water it hydrates and hardens.

It has thus been demonstrated that ordinary pure plaster of Paris of good quality is not anhydrous calcium sulphate, as hitherto considered, but a definite hydrate  $(\text{CaSO}_4)_x \cdot 2\text{H}_2\text{O}$ .

It has been shown by Debray, by experiments on hydrated salts, that their decomposition is limited to a given temperature by a definite vapour tension, and that the different hydrates of the same salt are characterised by different tensions at the same temperature. It was therefore concluded that the temperatures of decomposition of the two hydrates of calcium sulphate would be precisely those for which their vapour tensions are equal at atmospheric pressure, and consequently the temperature of decomposition would be lowered by diminishing the pressure. Experiment gave facts directly contradictory to these views, and, indeed, proved that the temperature of decomposition is completely independent of pressure. It follows, therefore, that the phenomenon of two stages of dehydration in this case is not one of dissociation. The temperature of dehydration was found to vary with rapidity of heating, and when operating on a large scale, M. Lacauchie, director of the plaster works at Argenteuil, gave the number  $125^{\circ}$ , which differs very little from that of Le Chatelier—namely,  $128^{\circ}\text{C}$ .

It is now ascertained that the temperature for baking gypsum differs from its temperature of dissociation, being always higher, that it is independent of pressure, that it is not theoretically capable of any precise definition, but that

it varies within small limits and lies between  $120^{\circ}$  and  $130^{\circ}\text{C}$ .

*ON THE SETTING OF PLASTER OF PARIS.*

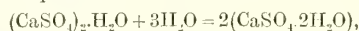
As Lavoisier stated, plaster of Paris which has been baked recombines with water when mixed therewith. The quantity of water added influences the setting of the plaster, but even a large excess does not prevent it. A mixture of no considerable consistency will harden in time if the plaster is good, the hardened mass becoming more porous than if mixed with a smaller proportion of water. It is generally admitted that when plaster sets there is not merely a process of hydration, but also a crystallisation of the hydrate. As the quantity of water, or more properly, of aqueous solution, in which the crystals can form is limited, the crystals interfere with each other and interlace, forming a confused mass. This account of the phenomenon is, however, incomplete, inasmuch as it accounts neither for the mass crystallising nor for the hardening of such a mass of crystals. Landrin (*Annales de Physique et de Chimie*, 5th series, 3, 441) has studied the question of the setting of plaster by the aid of the microscope, and his views may be summarised thus : 1. Burnt plaster in contact with water becomes converted into a crystalline hydrate; 2. Water which surrounds the crystals dissolves a certain proportion of the hydrated calcium sulphate; 3. The heat of chemical combination which yields the crystalline hydrate evaporates a portion of the water; a crystal is then formed, which determines the crystallisation of the whole of the dissolved sulphate. It may be remarked that for this action to take place it is necessary for the solution of calcium sulphate to be in a condition of supersaturation; a crystal of the hydrated salt would then act in the same way as a crystal of sodium sulphate containing 10 molecules of water when dropped into a supersaturated solution of the same salt. A sudden change from the liquid to the solid state occurs.

Now this theory renders evaporation an indispensable condition to the setting of plaster.

Le Chatelier (*Recherches Expérimentales sur la Constitution des Mortiers Hydrauliques*) recognises this point, and demonstrates the inaccuracy of such a theory by placing plaster mixed with water in a flask which, being hermetically sealed, admits of no evaporation. Nevertheless, the plaster sets as readily as if exposed freely to the air. He further remarks that the quantity of plaster which could thus crystallise by evaporation is a negligible quantity of the whole mass which sets.

Le Chatelier's views are as follows :

The chemistry of hydration being expressed by the equation



it appears from an experiment made by Marignac that the compound  $(\text{CaSO}_4)_x \cdot \text{H}_2\text{O}$  dissolves when shaken up with water and forms a clear solution, which after a short interval becomes turbid and deposits crystals with the composition  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The solution at first formed is five times as strong as that made from the dehydrated sulphate; it appears, then, that



what immediately enters into solution is the compound  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ —it becomes hydrated, its solubility is then diminished, and the solution becomes supersaturated with the salt  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . When the supersaturated solution has deposited its excess of crystals it dissolves more of the plaster  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ , and this after hydration is deposited in the same manner as the former quantity. The process is then repeated and continued until every particle of plaster has passed through the changes of solution, hydration, and crystallisation. When hydration is very slow the supersaturation is feeble; when it is rapid, supersaturation, on the contrary, is considerable.

If this explanation is correct, the points where crystals are formed are not necessarily where the solution is in contact with grains of plaster; and it is a fact that while plaster of Paris is setting under the microscope large needle-shaped crystals are seen to grow out of clear spaces filled with liquid, hence the plaster must have entered into solution before it became hydrated. An analogous case of solution of a dehydrated salt, followed by hydration, supersaturation, and crystallisation, causing the formation of a hard mass, is afforded by several very soluble substances. De Coppet (C. R. 73, 1324) has shown that anhydrous sodium sulphate yields solutions which are highly supersaturated even when care is exercised to prevent any rise of temperature in the liquid (Le Chatelier, *l.c.* 18). If a tube, about half an inch in bore and a foot long, be divided into an upper and a lower half, by placing within it a screen of wire-gauze, it may be filled with water, and the upper division charged with pieces of fused sodium sulphate the size of peas, which remain suspended in the liquid. To prevent rise of temperature the tube is immersed in water, and after some hours the hydrate  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  is deposited in crystals at the bottom of the clear solution, and these crystals grow until the tube is entirely filled with a hard mass.

That crystals in the form of delicate prisms are produced in the setting of plaster has been proved in many ways. 1. They have been observed under the microscope. 2. Plaster mixed with water containing alcohol sets so slowly that they are easily observed during formation. 3. Plaster mixed with potassium sulphate forms long prisms during setting, which are easily visible to the unaided eye.

Plaster contains 7 to 8 p.c. of combined water, and the proper quantity of water required to make plaster set properly may be calculated from the foregoing equation as about 13 parts for 100 of ordinary plaster; if the quantity taken be so small as even 33 parts for 100 of plaster the setting follows so rapidly, almost instantaneously, that it is useless. That is to say, it is necessary to add at least more than 20 p.c. over the calculated amount because the plaster itself is porous and it dries rapidly.

If gypsum be *over burnt*, that is to say, dehydrated completely, it will not set in the usual manner when mixed with the proper quantity of water. Landrin has shown that if a minimum of water be used, say 33 p.c., then the plaster will set to unusual hardness after a lapse of some twelve

hours. If over-burnt plaster be exposed to the air it absorbs 8 p.c. of water very rapidly, but further hydration proceeds very slowly. Such plaster when properly mixed with water sets slowly, but with a normal hardness.

These facts are readily understood when we consider that the compound  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$  is the only calcium sulphate which sets properly. It is evident that the mode of crystallisation which occurs in the setting of plaster must influence its hardness. Le Chatelier states that the crystals which form are frequently, if not always, little delicate prisms united by one of their ends round central points so as to build little spherical concretions. Le Chatelier considers that the mechanics of hardening of mortars and cements can scarcely be without analogy, and may possibly be identical in operation, with other known modes of hardening. These are hardening by *compression* of a powder, by *desiccation* of a powder or colloid substance such as gelatine, by *fusion* and *solidification*, by crystallisation.

These may be referred to two simple and more general phenomena:

*Mutual adhesion* of solid particles, brought within a minute distance of each other;

*Mobility* of these particles enabling them to approach.

In the case of plaster of Paris mobility is conferred upon the particles by their being dissolved previous to crystallisation; they are brought close together by the solution being supersaturated. As soon as crystallisation has taken place, the crystalline mass will be so much the harder the greater the internal *cohesion* of the crystals and the greater their mutual adhesion.

*Cohesion*, which is a primordial property of matter, is widely extended. Plaster can be scratched by the nail; quartz is so hard as to scratch steel. *Adhesion*, unlike cohesion, is a complex phenomenon, and consequently very variable. These variations almost entirely account for the difference in hardness which analogous cements and mortars present. *Adhesion* varies with the *chemical nature* of the substances in contact. The adhesion of a crystal of calcium sulphate to a plate of glass is *nil*; on the contrary, that of barium silicate is so great that the crystals break rather than become detached therefrom. It varies with the more or less polished state of the surfaces in contact.

The total effect of adhesion is evidently proportional to the extent of surfaces in contact. It is so much the greater as—first, the volume of empty spaces arising from excess of water used in the mixing is less; secondly, as each crystal for a given weight of matter affords a greater development of surface—the form of elongated prisms recognised by Le Chatelier in crystals of plaster and all similar products is eminently favourable to adhesion; thirdly, crystals should be so grouped as to increase the volume of the empty spaces while diminishing their number and isolating them from each other. A structure like pumice is particularly favourable. But very slight variations in external conditions, such as the nature of the solvent, the temperature, and the number of points or rough surfaces from which crystallisation may be favoured, exert a considerable difference on the strength of mortar, plaster, and cements.

## PROCESSES FOR HARDENING PLASTER.

*Alum plaster.* Several new plastic substances have lately come into use, called *alum plaster*, *French cement*, and *English cement*, or *stucco*.

Greenwood's process is carried out in the following manner. Plaster stone, previously burnt in the usual manner, is steeped in a solution containing from 8 to 10 p.c. of alum. After soaking for some minutes it is drained, and dried in the air. It is then submitted to another burning at a uniform and constant temperature carried to dull redness, but not exceeding this limit.

Such plaster softens in water, so that it easily takes an impression from the fingers. Recently a material has been prepared by baking an intimate mixture of raw plaster with powdered alum.

Castings executed in such plaster solidify gradually, but they finally acquire a hardness similar to that of alabaster or marble; furthermore, the

material presents a translucent appearance which causes it to resemble these substances. Exposed for months to the air, the casts remain uninjured and lose none of their hardness. According to Elsner, several hours in boiling water does not sensibly affect their hardness.

Various explanations have been given of the cause of this change in plaster, but according to Landrin (C. R. 1874), it is not to be accounted for by the formation of double sulphates of lime and alkali, nor by the crystals of calcium sulphate being imbedded in alumina, but rather by the calcium carbonate in the plaster stone being converted by the alum into calcium sulphate. A liquid containing 8 to 10 p.c. of sulphuric acid acts as satisfactorily as an alum solution.

Specimens of such cements have been analysed and shown to be almost pure calcium sulphate. Compare the following two series of analyses of plasters:—

*Landrin's Analyses of Alum Plasters.*

Description of specimens	Constituents found				
	CaSO <sub>4</sub>	CaCO <sub>3</sub>	SiO <sub>2</sub>	H <sub>2</sub> O	Total
Alum plaster, French cement . . .	96.75	1.05	0.72	1.18	100
" " English cement, No. 1 . . .	98.19	0.41	0	1.40	100
" " " " No. 2 . . .	98.02	0.37	0.42	1.19	100
" " Stucco . . .	98.05	0.36	0.51	1.08	100

The following is a tabulated statement of the analyses of various kinds of plaster used throughout France, from which it will be seen that they

contain varying but considerable proportions of earthy carbonates.

*The chemical Composition of various kinds of Plaster of Paris.<sup>1</sup>**Analyses of Plaster of Paris made by M. Durand-Claye.*

Nature and source of the plaster	Constituents found					
	Residue insoluble in acids	Al <sub>2</sub> O <sub>3</sub> and Fe <sub>2</sub> O <sub>3</sub>	CaSO <sub>4</sub>	CaCO <sub>3</sub>	MgCO <sub>3</sub>	H <sub>2</sub> O
Vitry (Seine), ordinary . . . . .	4.9	2.5	70.9	10.2	5.05	6.15
" " fine . . . . .	3.7	2.7	72.6	12	5.45	3.55
Villejuif (Seine) . . . . .	4.8	0.6	77.95	8.5	1.9	6.25
Bondy (Seine), ordinary . . . . .	1.4	1.5	79.05	9.9	2.3	5.85
" " fine . . . . .	2.4	1	83.4	6.9	2.3	4
Romainville (Seine) . . . . .	0.6	0.8	87.7	2.4	2.7	5.8
Bois le Comte (Seine et Marne) . . . . .	1.2	0.35	85.75	4.3	—	8.4
Lamarche . . . . .	1.6	—	88.45	3.75	—	6.2
Bussière . . . . .	1.05	0.45	84	7.15	0.4	6.95
Roquevaire (Bouches du Rhone) . . . . .	11.2	3.1	70.55	6.7	5.65	2.8
Bassin de la Conze (Dordogne) . . . . .	4	1.4	71.60	14.1	5.05	3.85
Hérépian (Hérault) . . . . .	4.2	1	81.6	—	—	13.2
Partel (Aude) . . . . .	0.7	0.4	86.85	5.3	—	6.75
Malancène (Vaucluse) . . . . .	0.6	—	92	0.35	—	6.15
Poligny (Jura) . . . . .	0.8	—	93.5	3.4	—	2.3
Grasse (Alpes-Maritimes) . . . . .	0.1	0.2	95.65	—	—	4.05

<sup>1</sup> Encyclopédie Chimique, Fremy. Article Mortiers et Ciments, par M. Duquesnay, p. 173.

*Stucco.* A mixture of plaster with a solution of size; when hardened can be polished. This is called *stucco*. By mixing with the size certain metallic compounds, such as ferric hydrate, chromic oxide, manganic oxide, cupric hydrate, and basic cupric carbonate, *stucco* may be made of different colours. By appropriate treatment

the appearance of coloured marbles may be given to the *stucco*.

*Keene's cement.*—Keating, and previously Keene, have produced hard cements by mixing plaster of Paris with 1 part of borax and 1 part of cream of tartar with 18 parts of water. After the plaster is impregnated with the solution it is

dried and burnt at a low red heat for six hours. Borax alone answers the purpose equally well. The plaster hardens more slowly as the solution is more concentrated. By using 1 volume of a saturated solution of borax and 12 volumes of water, the plaster sets in a quarter of an hour; with 8 volumes of water, it sets in an hour; and with 4 volumes of water, setting is delayed for several hours.

**Silicated plaster.** Knauer and Knop sponge over the surface of plaster casts a solution prepared thus. To a potash ley made by adding 1 part of potash to 5 of water some milk-whey is added, as free as possible from fatty matter; 4 parts of this are mixed with a syrupy solution of potassium silicate. Dark stains sometimes appear on the surface, caused by the action of sulphur in the whey upon iron compounds in the plaster, but these disappear upon drying.

The application endows the plaster with great hardness and with an agreeable tone, far superior to its usually chalky appearance.

Stearine melted at not too high a temperature has been employed as a bath in which plaster casts are immersed. The porosity of the plaster enables it to absorb a certain quantity of the stearine which solidifies on cooling.

**4. Hydraulic Mortars.** All mortars which set under water or in damp places are said to be hydraulic. They may be divided into three classes:

1. Ordinary hydraulic mortars, composed of hydraulic lime and sand.
2. Mortars made with 'fat' lime or hydraulic lime and pozzuolana, with or without sand.
3. Mortars made with slow or quick-setting cements, with or without sand.

Natural limestones, which on being calcined are capable of forming a mortar which possesses the important property of hardening under water and of resisting its continued action, are called hydraulic limestones, and limes prepared therefrom are hydraulic limes. The real cause of such water-setting and resisting properties of mortars and cements was discovered and applied by the engineer Smeaton about the year 1756.

It is worth while to emphasise the importance of this discovery by a quotation: 'Smeaton overset the prejudices of more than 2,000 years, adopted by all former writers, from Vitruvius in ancient Rome to Belidor in France and Sempio in this country, who agreed in maintaining that the superiority of lime consisted in the hardness and whiteness of the stone, the former of which may or may not be accompanied by water-setting properties, and the latter of which is absolutely incompatible with them' (Preface to Sir C. N. Pasley's *Observations on Limes, Calcareous Cements, Mortars, Stuccos, and Concrete*).

When limestones contain clay, or in certain cases magnesia, they yield hydraulic limes.

**Silicated mortars.** The following table, prepared by Durand-Claye from the analyses of Vicat and Berthier, indicates the degree of hydraulicity belonging to limes with different degrees of impurity in the form of clay.

These limes are distinguished from 'fat' and even from 'poor' limes by slaking more slowly, with only a slight rise of temperature and but

little or no disengagement of vapour. This increase in volume rarely exceeds one-third their original bulk. They harden under water if made into a paste, at periods which may be 15 or 20 days after immersion if slightly hydraulic; 6 to 8 days if hydraulic; and 1 to 4 days if highly hydraulic.

Proportion of clay to 100 parts of calcium carbonate in the limestone.

Lime feebly hydraulic contains	5.3 to 8.2
" fairly "	8.2 to 14.8
" hydraulic "	14.8 to 19.1
" highly hydraulic "	19.1 to 21.8
Limit of hydraulic lime	21.8 to 26.7

(Dictionnaire de l'Industrie, E. O. Lamic, 1883.)

Usually hydraulic mortar is prepared from a silicious limestone, such as would fall under the description before given, or from a mixture of a 'fat' lime with silicious materials such as pozzuolana.

Three very important works have been constructed with lime the composition of which is known, namely, the old Eddystone Lighthouse, erected by Smeaton, the Liverpool Docks, and works on the Suez Canal at Port Said.

Mortar for the Eddystone Lighthouse was mixed with one of the strongest of hydraulic limes from Aberthaw in Glamorganshire. It contains:

*Aberthaw Limestone.*

Calcium carbonate	86.2 p.c.
Clay	11.2 "
Water, alkalis, &c.	2.6 "
	100.0

*Composition of Hydraulic Mortars.*

Description of Mortar	Aberthaw lime Slaked Powder	Pozzuolana	Sand
	bushels	bushels	bushels
1. Eddystone	2	2	
6. Stone mortar	2	1	1
3. Ditto, 2nd quality	2	1	2
4. Face mortar	2	1	3
5. Ditto, 2nd quality	2	$\frac{1}{2}$	3
2. Backing mortar	2	$\frac{1}{4}$	3

Mortar for the Liverpool Docks was prepared from blue lias obtained near Holywell, Flintshire, N. Wales.

*Blue Lias Lime (Muspratt).*

Calcium carbonate	71.55 p.c.
Magnesium carbonate	1.35 "
Alumina	3.52 "
Silica	20.10 "
Ferric oxide	2.21 "
Alkalis	0.79 "
Water and loss	0.50 "

99.82

Constituents soluble in hydrochloric acid	74.73 p.c.
Insoluble	25.27 "

100.00



*Hydraulic Mortar for Liverpool Docks.*

	Slaked Lias Lime	Sea Sand	Furnace Ashes
1st Quality	1 measure	1 measure	$\frac{1}{4}$ measure
2nd Quality	1 „	2 measures	$\frac{1}{4}$ „

In each case the burning and slaking of the lime was most carefully attended to, and the mortar received the most careful manipulation.

The Port Said Canal works, were constructed of concrete blocks made with Theil lime, in the proportion of 325 kilos. of lime in a dry powder to 1 m. 3 cm. of sand.

*Composition of Lime from Theil (Ardèche, France).*

Lime	. . . . .	65.10 p.c.
Magnesia	. . . . .	0.65 „
Silica combined	. . . . .	19.05 „
Silicious sand	. . . . .	0.30 „
Alumina	. . . . .	1.60 „
Ferric oxide	. . . . .	0.55 „
Sulphuric acid	. . . . .	0.30 „
Loss on burning	. . . . .	12.15 „
		100.00

The setting of hydraulic mortars will be dealt with under hydraulic cements.

*Dolomitic mortars.*—Sir Charles Pasley was the first who discovered that calcined magnesium carbonate was in itself a slow-setting cement. Deville has shown that dolomites yield a lime which has the property of forming hydraulic

mortars, and Crace-Calvert has furnished analyses of several such stones.

*Analysis of Dolomitic Limestones (Crace-Calvert).*

—	From Craig Bract	Port Eynsor	Hell's Mouth
Magnesium carbonate	61.15	55.23	15.86
Calcium carbonate	21.41	33.99	72.23
Ferrous carbonate	8.76	3.85	3.21
Silica . . . . .	5.58	5.58	} 2.7
Alumina . . . . .	2.07	2.27	
Organic matter and water . . . . .	1.10	3.40	6.0
	100.07	104.32	100.00

**5. Pozzuolana.** Pozzuolana is, strictly speaking, a mixture of silicates of volcanic origin, originally discovered at the foot of Mount Vesuvius, near the village of Pozzuoli. A large proportion of the silicates are decomposable by hydrochloric acid. For purposes of construction, when mixed with 'fat' lime, its valuable properties have been known for centuries. Vitruvius and Pliny described it, and extensive Roman works in which it was employed are standing at the present day. The mortar described by Vitruvius, with slight variations, is

*Analyses of Pozzuolani and Trass (Vicat and Hervé-Mangon).*

Source	Constituents p.c.							
	Mixed sand	Silica	Alumina	Ferric oxide	Lime	Magnesia	Water	Not esti- mated, or volatile matter
Vesuvius, brown . . .	2.50	44	10.5	29.5	10	traces	2.5	1
„ dark grey . . .	1.5	44.5	16.5	15.5	10	3	3	6
„ light grey . . .	2.5	42	15.5	12.5	9.5	4.4	3.33	10.27
„ lava, 1868 . . .	—	39	14.0	13.0	18.0	3.0	—	11.0
Rome, St. Paul's Caves .	5	47.66	14.33	10.33	7.66	3.86	7.03	4.13
Auvergne, black . . .	0	47.9	34.20	8.2	3.9	3.2	—	2.6
„ reddish brown . .	—	47.1	39.0	7.0	trace	2.2	—	4.7
„ brick red . . .	—	46.05	17	20.55	8.55	trace	1.6	6.35
„ Gravenvère . . .	—	48.0	36.40	8.10	trace	—	2.4	4.80
Trass, Andernach . . .	—	48.94	18.95	12.34	5.41	2.42	—	11.94
„ Dutch . . . . .	—	46.6	20.6	12.0	3.0	—	12.8	5.0
„ Rhenish . . . . .	8.75	46.25	20.71	5.48	2.15	1.0	9.25	6.3

used very generally throughout Italy and at Toulon and other French ports. Its composition is as follows:

- 12 parts of pozzuolana, finely powdered.
- 6 „ quartzose sand, well washed.
- 9 „ 'fat' lime, recently slaked, to which is added
- 6 „ fragments of broken stone, porous and angular.

Varieties of pozzuolana may exist in all volcanic localities.

*Trass.* On the Rhine the Romans are supposed to have used, instead of pozzuolana, a volcanic product of the Eifel district called tufa. The Dutch used the same material, and called it *trass*, or *tyrass*, which means a binding or adhering substance. It has been employed

on hydraulic works for more than 200 years, for in 1682 Van Santen erected a mill on the Rhine for grinding trass. This material is shown by the table of analyses given above to be substantially of the same composition as pozzuolana.

*Santorin earth.*—Another useful description of tufa covers the entire island of Santorin (the ancient Thera), in the Greek Archipelago. From time immemorial, up to as recent a date as 1866, this island has been subject to volcanic disturbances. The earths obtained therefrom are valuable for the making of cements, and they are undoubtedly similar in character to pozzuolana and trass, but they consist of an active cementing material, a fine grey earth consisting of partially hydrated silicates, mixed with pumice and particles of obsidian, which have no more

action than sand. Each analysis shows that Santorin earth differs from pozzuolana and trass chiefly by containing a much larger proportion of silica and less lime. Santorin earth has been used for a long time on the shores of the Mediter-

anean. It was largely employed in hydraulic structures at Trieste, Venice, and Fiume. Elsner says that so long as it is immersed Santorin mortar remains hard, but when dried in the air it soon crumbles away.

#### *Analysis of Santorin Earth (Feichtinger).*

- I. Portion which floats on water, and is  $\frac{1}{20}$ th of the whole, consisting of pumice.  
 II. The greater portion of the earth, a fine light grey powder, which can be separated from III. by levigation.  
 III. Consisting of particles of obsidian of various colours, and with sharp edges.

—	I. Pumice		II. Fine particles		III. Coarse particles	
Constituents soluble in HCl:						
Lime . . . . .	0.40		0.84		0.68	
Magnesia . . . . .	0.25		0.48		0.35	
Ferrie oxide . . . . .	0.28		0.54		1.86	
Alumina . . . . .	0.75		1.31		1.64	
Silica . . . . .	trace	1.68	trace	3.17	trace	4.53
Constituents insoluble in HCl:						
Silica . . . . .	72.84		71.44		63.07	
Lime . . . . .	2.15		1.80		3.15	
Magnesia . . . . .	1.33		1.36		1.58	
Alumina . . . . .	11.51		8.56		14.03	
Ferrie Oxide . . . . .	4.07		3.30		6.87	
Potash . . . . .	1.28		1.86		1.87	
Soda . . . . .	2.65	95.83	3.74	92.06	3.86	94.13
Water . . . . .	2.25	2.25	4.61	4.61	1.14	1.14
	99.67		99.84		100.10	

Silica soluble in dilute caustic alkali was present in the following quantities:

- I. 5.2 p.c. II.\* 28.4 p.c. III. 3.4 p.c.

*Arènes*.—A species of ochreous sand which goes by this name is found abundantly in France, in the Department of Dordogne, and in several localities on the tributaries of the Loire and the Somme. On account of the large proportion of clay which many of them contain, they can be formed into a paste with water without any addition of lime, and are often used in that state for the walls of buildings as well as for mortar. Mixed with 'fat' limes they give excellent mortars, which gain great hardness under water. In rapid setting they compare favourably with the most energetic hydraulic lime. The property of quickly setting is greatly increased by burning.

#### *Analysis of Arènes from St. Astier, Dordogne (Vicat):*

Mixed sand . . . . .	4.13 p.c.
Silica . . . . .	38.54 "
Alumina . . . . .	20.0 "
Ferrie oxide . . . . .	12.0 "
Lime and magnesia . . . . .	4.8 "
Water . . . . .	17.0 "
Volatile matter and loss . . . . .	3.85 "

100.32

*Artificial Pozzuolane*. Many substances of natural occurrence which do not possess hydraulic properties may, by burning, be converted into what may be termed artificial pozzuolane; that is to say they form quick-setting hydraulic mortars if mixed with 'fat' lime.

\* II. This is the portion which forms the binding material when mixed with lime, while I. and III. merely play the part of sand in mortar.

Such substances are:—

- Baked clay.*
- Burnt schist.*
- Calcined basalt.*
- Sand and burnt arènes.*
- Argillaceous sandstone.*

Ordinary clay consists of silicate of alumina more or less mixed with calcium carbonate and ferrie oxide. When heated to dull redness or between 600 and 700°C., it acquires hydraulic properties. It is essential that it be exposed to the air during heating, and that the carbonic acid be expelled from the calcium carbonate and the combined water from the clay. The temperature should not exceed 700 or 800°C. (Vicat). Many Roman structures in Britain appear to have been built with mortar made of such materials.

Blue schist burnt in a lime kiln becomes converted in friable porous masses of a pale-green colour (Baggi).

Basalt calcined in a kiln until it commences to flux is converted into a pozzuolana (De Cessart).

*Sand and baked arènes*. In some places sand and arènes are found adjoining or mixed. Their property of setting is much improved by baking.

*Argillaceous sand*. In the neighbourhood of La Fère, M. Ménard has found sand with an argillaceous gangue which acquires the properties of pozzuolane by baking on an earthenware plate at a moderate temperature.

**6. Hydraulic Cements.** Hydraulic cements are of two kinds. Those which may be called natural cements are formed by burning a natural product such as an argillaceous limestone unmixd with lime in the works; artificial cements are such as may be obtained by burning

a mixture of chalk or 'fat' lime with clay. In 1796 James Parker obtained a patent for working up argillaceous limestones, found near London, into a quick-setting cement, called by a trade name 'Roman cement.'

*Roman cement.* This cement is formed by burning *septaria*, or clay nodules found on certain parts of the coast of Kent and Essex. When calcined and pulverised, *septaria* are in a suitable condition to be employed as mortar for hydraulic purposes. The Thames Tunnel was in fact built by the aid of such mortar, and indeed until the introduction of Portland cement in 1824, it was universally used for engineering and other works at home and abroad. This cement has since been made in several parts of England and Scotland, and the original name having been dropped, local names have been given to the cements. Knauss has investigated some of these by analysing the material from which they are prepared, the cement ready for use, and cubes of the cement after it has set. Such cement requires much care in its preparation and great outlay for plant. It deteriorates somewhat by keeping, but it is particularly suitable for work wherein great expedition is necessary or desirable. The Thames Tunnel would not have been built if this material or a similar quality of cement had not been easily procurable.

The great end to be attained in the production of Roman cement is complete expulsion of carbon dioxide from the limestone or chalk. This is indicated when the stone is reduced to a minimum of weight, so that there is a maximum of burnt lime and no trace of vitrification from over-heating. When freshly ground it should never exceed 80 lbs. per imperial bushel. Thorough pulverisation is essential.

*Medina cement.* This is a variety of the former, made from a stone found in the Isle of Wight; it possesses in high degree the property of quickly setting. Such cements are valuable for protecting joints, made with slowly setting Portland cements, from the action of the waves and running water.

Knauss's analyses are given on the following page. It may be remarked that they are valuable for the reason that they give the composition of the stone, of the cement made therefrom, and of cubes formed from the cement; which is important, since limestones from the same quarry and cements from the same source sometimes have a different composition.

Gätschenberger analysed a cement from the neighbourhood of Heidelberg with the following result:

	p.c.
Lime . . . . .	41.22
Magnesia . . . . .	17.77
Ferrie oxide . . . . .	3.07
Alumina . . . . .	5.75
Manganous oxide . . . . .	2.33
Alkalis . . . . .	4.72
Silica . . . . .	22.14

---

100.00

The stone from which this cement is prepared by burning can be made to yield two products, according as it is burnt at a low or a

high temperature. (1) When burnt at a temperature below 400°C. the magnesia is rendered caustic, but not the lime. (2) When the stone is burnt at a high temperature it almost fuses.

In (1) the conditions are such that magnesia acts as the hydraulic agent, while in (2) it is the silicates of lime and magnesia. An excellent cement burnt at a high temperature contained 100 ( $\text{SiO}_2 \cdot \text{R}_2\text{O}_3$ ), 304 ( $\text{CaO} \cdot \text{MgO}$ ); the proportion 100 ( $\text{SiO}_2 \cdot \text{R}_2\text{O}_3$ ), 304 CaO would be almost useless.

#### THE PROCESS OF MAKING CEMENTS.

*Portland cement.* This is a material of artificial origin, produced by baking a judicious mixture of chalk and fine clay of a peculiar nature. Unlike Roman cement, it is most valuable when heaviest, and it furthermore differs in its slowness of setting. These cements of greatest density set the slowest, and ultimately acquire the greatest amount of strength and hardness. The name Portland cement was given to it by the inventor, John Aspdin, of Leeds, in 1824, from its close resemblance, when set, to the stone from the Portland quarries. The process of manufacture was as follows. Quicklime in powder was mixed with an equal weight of clay and kneaded with water into a plastic mass. It was dried, broken in pieces, and burnt in a limekiln till all carbon dioxide was expelled. After being reduced to powder it was ready for the market. Sir Charles Pasley must, however, be considered the founder of the cement industry in England. In the year 1826 he obtained a cement by burning river mud from the Medway, impregnated with the salts from sea-water, with an admixture of limestone or chalk. There is little doubt but that the sodium salts are converted into silicates, together with the lime, and the alumina of the clay becomes calcium aluminate, and that the sodium silicate is of benefit in the setting of the cement. At the present day the mud of river mouths and delta formations is largely employed for the purpose of making cement.

The process of making Portland cement is usually as follows. Chalk or limestone, and clay or river mud, in equal proportions, are intimately mixed, the mixture is dried in the air, and then burnt in a shaft kiln. The kiln is 40 to 90 feet high, and 7 to 12 feet in diameter. At 4 feet from the ground is a strong grating, through which lumps of limestone mostly fall. The kiln is so arranged that fuel and cement stone occur in alternate layers. Coke is the best fuel. After heating to redness for an hour, the mass assumes a yellow-brown colour, and at a higher temperature it becomes dark brown. Gradually the lime becomes causticised, and attacking the clay becomes converted into a calcium silicate and calcium aluminate. At a white heat the mass becomes grey in colour, with here and there a streak of green. Beyond this stage the powder is blue-grey or greyish white, clear and sharp, and very similar to glass powder. The more basic the mixture the more durable the cement. A mixture in which clay predominates is always more or less a weak cement. The more intimately the lime and clay are mixed the better is the cement, because a greater amount of lime is converted into sili-



*Analyses of Hydraulic Cement Stones and Cements (Knauss).*

	I. Limestone			II. Limestone		
	Unburnt	Burnt	Set Cubes	Unburnt	Burnt	Set Cubes
Constituents insoluble in HCl:						
A { Quartz . . . . .	(a) 6.0	(b) 6.2	(c) 8.4	(a) 12.3	(b) 8.3	(c) 3.1
Silica . . . . .	10.5	0.3	3.8	9.0	0.5	1.2
Ferric oxide . . . .	1.2	1.3	2.5	1.9	1.7	0.6
Alumina . . . . .	2.5			2.4		
Insoluble constituents .	20.2	7.8	14.7	25.6	10.5	4.9
Constituents soluble in HCl:						
Silica . . . . .	0.7	19.4	8.4	0.6	17.4	17.6
Ferric oxide . . . .	11.6	9.2	6.6	6.3	12.4	9.5
Alumina . . . . .	4.3	7.3	5.9	1.1	4.6	6.6
Lime . . . . .	29.3	48.2	42.8	32.4	46.1	36.6
B { Magnesia . . . . .	3.3	2.7	1.9	2.7	3.7	1.7
Potash . . . . .	0.8	0.8	1.0	0.9	0.9	1.1
Soda . . . . .	0.2	0.2	0.3	0.2	0.1	0.2
Carbon dioxide . . .	26.8	3.4	11.8	28.4	3.6	13.5
Water . . . . .	2.8	1.0	6.9	1.8	0.7	8.3
Soluble constituents .	79.8	92.2	85.3	71.4	89.5	95.1
Total . . . . .	100.0	100.0	100.0	100.0	100.0	100.0

Ia. Moderately hard, yellowish brown limestone richly studded with calespar, Kent.

Ib. Sheppy cement prepared from Ia.

Ic. } Cubes prepared from Ib and IIb.

IIa. A limestone similar in appearance to Ia, from Essex.

IIb. Harwich cement from IIa.

	III. Limestone.			V.		
	Unburnt	Burnt	Set Cubes	—	—	—
Constituents insoluble in HCl:						
A { Quartz . . . . .	(a) 9.2	(b) 11.0	(c) 7.8	a { 4.6 3.2		b 4.9
SiO <sub>2</sub> . . . . .	8.1	2.8	1.2	6.6	4.1	1.3
Fe <sub>2</sub> O <sub>3</sub> . . . . .	2.1	2.4	0.4	2.2	2.1	1.2
M <sub>2</sub> O <sub>3</sub> . . . . .	3.8			2.5	1.8	1.3
Insoluble constituents .	23.2	18.2	9.4	15.9	11.2	8.7
Constituents soluble in HCl:						
SiO <sub>2</sub> . . . . .	0.5	9.1	9.2	1.4	0.8	11.9
Fe <sub>2</sub> O <sub>3</sub> . . . . .	2.3	7.1	6.1	1.7	3.1	3.6
Al <sub>2</sub> O <sub>3</sub> . . . . .	1.6	9.8	9.5	3.1	0.8	5.6
CaO . . . . .	38.5	49.6	40.0	35.3	40.2	47.4
B { MgO . . . . .	1.1	1.6	1.6	5.9	4.4	9.4
K <sub>2</sub> O . . . . .	0.7	0.8	1.0	0.8	1.1	1.5
Na <sub>2</sub> O . . . . .	0.3	0.2	0.2	0.4	0.3	0.3
CO <sub>2</sub> . . . . .	31.4	2.7	14.4	34.2	36.4	11.0
H <sub>2</sub> O . . . . .	0.4	0.9	8.6	1.3	1.7	0.6
Soluble constituents .	76.8	81.8	90.6	84.1	88.8	91.3
Total . . . . .	100.0	100.0	100.0	100.0	100.0	100.0

IIIa. A bluish-grey hard limestone from Yorkshire.

IIIb. Whitty cement from IIIa.

Va. Two limestones from Horb in Würtemberg.

Vb. Hydraulic lime from Va and b.

cate and aluminate. Portland cement mixed with water stiffens in a few minutes, and after the lapse of a day is tolerably hard. After a month it becomes so hard that it emits a sound after being smartly struck.

The form of kiln used in burning cements is generally in section that of two truncated cones with the broad base of the one applied to that of the other. See figs. 18, 19, and 20.

Their capacity usually admits of 25 to 30 tons of cement being burnt at each firing.

The period of firing continues from twenty-

four to fifty hours, and that of cooling for two to three days. They are lined with refractory fire-bricks, very solidly constructed and braced together with iron hoops or bars. The temperature they have to withstand is much higher than that of a lime-kiln.

In fig. 18 are shown the elevation and vertical section of the cement-kilns of MM. Demarle and Linquety in use at Boulogne. In the baking of cements much carbon monoxide and sulphur dioxide are produced, and in order to remove these noxious gases the kiln shown in figs. 19 and 20 is

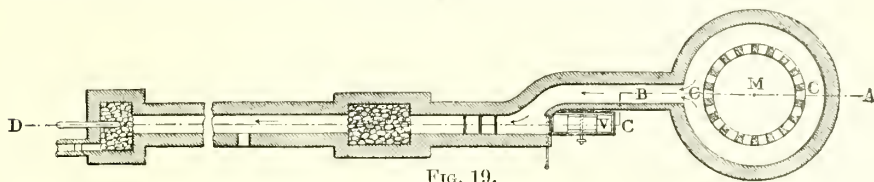


FIG. 19.

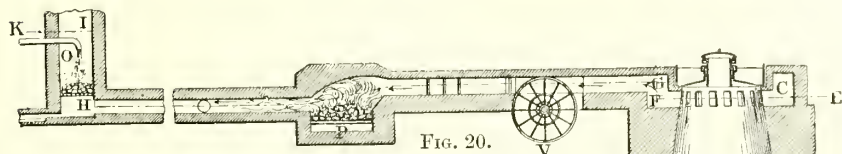


FIG. 20.

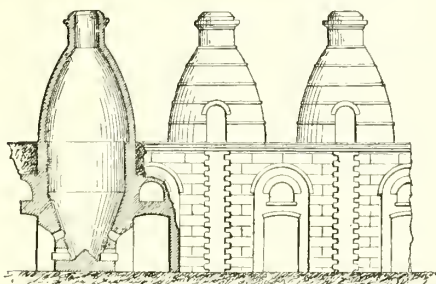


FIG. 18.

in use at the works of Mr. Campbell, Wouldham Valley, Kent. The body of the kiln *M* is inclosed, below the covered head the peripheral wall is perforated and the gases escape into a surrounding circular channel *c c*. A passage *B* or *F, G, H*, leads from this channel to a coke fire *P*, and thence to a packing of coke in the flue *II*, over which water from a pipe *O*, drips and removes much of the sulphurous gas. The carbon monoxide being present in large proportion is burnt at the coke fire *P* by air admitted by the ventilator *V*.

The following interesting account of cement manufacture is taken from the Engineer, vol. liv. p. 98, 1882 :

'In the new harbour works of the South-Eastern Railway Company, at Folkestone, artificial blocks, made of pebbles from the sea beach, bound together with Portland cement, are largely used. The Portland cement is obtained from the Folkestone Cement Works, about half a mile from the harbour, the raw materials being obtained close by. The works

stand upon an inclined plane; chalk is brought from the cliffs above, and clay is wound up to them by a stationary engine, from a clay-pit 100 or 200 yards from the place of manipulation.

'The materials for the manufacture of Portland cement vary in different districts. On the Thames, white chalk and alluvial mud found in the marshes adjoining the Medway are used; on the Medway, grey chalk and the same mud; in the lias districts, the limestone shales and clays of the deposits are the most suitable. At Folkestone grey chalk and the gault clay which underlies the grey chalk, as already stated, are the raw materials.

'At Folkestone the different beds of grey chalk and gault clay vary considerably in composition. When free from water the chalk contains from 84 to 95 p.c. of carbonate of lime, the rest being clay; and the clay, in a dry condition, contains from 10 to 30 p.c. of carbonate of lime. The chalk upon an average

contains 20 p.c. of water, the clay 25 p.c. The first object to be attained is to reduce these substances to a fine state of division, and at the same time intimately mix them together in such proportions that when deprived of water the mixture shall contain from 75 to 76 p.c. of carbonate of lime. This is done by what is known as the wet process. The raw materials are fed in measured proportions into a wash-mill, which is a circular trough in which a number of harrows revolve, driven by a steam engine of 14 h.p. A stream of water is constantly flowing in, and the action of the harrows, aided by the attrition of the particles against each other, reduces the whole to a state of "slurry" or slip, which contains from 60 to 70 p.c. of water. In this state it flows into the settling tanks or "backs," each of which contains sufficient slurry to make 800 tons of cement. Here it is allowed to subside, the supernatant water being drawn off from time to time. One settling tank is filled at a time, and then left for six or seven weeks for the solid matter to settle, the surface water meanwhile being drawn off from time to time by a small sluice. The bottoms of the tanks are of the natural porous earth of the locality, and help a little to drain off the water by absorption.

'To return to the wash-mill. No coarse particles of chalk must be allowed to pass into the backs, as their presence would endanger the cement. To guard against this the slurry is caused to flow away from the wash-mill through strainers of fine copper-wire gauze. Catchpits are placed between the strainers and the backs to intercept any coarse particles that may have escaped. The process is a continuous one, a stream of water with successive charges of chalk and clay constantly going in, and a stream of slurry continually flowing out. The rate of flow has to be carefully regulated, so as to secure a proper mixture. Some of the beds of clay are easily washed down, while others are most tenacious and difficult to break up. Some of the chalk is soft and is easily washed; other beds, notably that called the "burr chalk"—which is a kind of junction bed between the upper and lower chalk deposits—are harsh and gritty in the breaking up. The mechanical condition of the slurry is continually examined during the process of washing, by washing a small known quantity through a fine sieve, and drying and weighing the residue. The composition of the raw materials being known, their accurate mixture in the required proportion is simply a matter of calculation. To guard, however, against possible error, the percentage of carbonate of lime in the slurry is constantly determined. If the percentage is not correct the proportions are altered, while occasional stirring of the backs ensures a uniform product. Many methods of analysis may be adopted. The lime may be determined directly, but the operation involves much time and tedious work, especially where, as in a cement works, many determinations have to be made. For all practical purposes a determination of carbonic acid in a dried and gently ignited sample of the slurry is sufficient. From this the percentage of carbonate of lime can be readily calculated.' A form of apparatus which gives the required result in

from fifteen to twenty minutes, and involves only one weighing, viz. that of the quantity taken for the determination, is Scheibler's Calci-meter. The carbonic acid displaces an equal volume of air which is collected over water, its volume read off, and the weight of an equal volume of carbonic acid is calculated, with the usual corrections for temperature and atmospheric pressure. Another method, which is very accurate, is to absorb the carbonic acid in a U tube filled with potash-pumice, or soda-lime, the tube being weighed before and after the operation. 'When sufficiently still to be dug out, the slurry, still containing from 40 to 50 p.c. of water, is removed from the backs in waggons to the drying floor. This is heated by the waste gases from a range of coke ovens, in which just sufficient coal is coked to dry sufficient slurry in twenty-four hours to load one kiln. The kilns are seven in number, from each of which 18 tons of cement clinker are drawn. The process of burning is an intermittent one. The kiln is charged with alternate layers of coke and dry slurry, lit at the bottom by means of thirty baskets of coke laid upon brushwood faggots. These kilns are subject to great wear and tear, but injury is materially lessened by coating their sides with slurry before each charging. A charge is usually burnt off in thirty-six hours, after which it is allowed one or two days to cool. The charge is then drawn. The fuel and slurry are distributed in the kiln according to the judgment of the burner. At these works one ton of cement is burnt with twenty bushels of coke.

'It may be mentioned here that slurry prepared with a somewhat lower percentage of carbonate of lime than that previously mentioned, say from 72 to 73 p.c., would require less fuel to burn it, and the resulting clinker would be more easily ground, but the cement would have a low tensile strength. On the other hand, a higher percentage would largely increase the quantity of fuel required, give a dense hard clinker very difficult to grind, and the cement would be liable to crack, and fly when used. The product from the kilns is a hard blue-grey clinker, from which all underburnt portions are carefully picked out. The clinker is crushed by one of Hall's multiple action stonebreakers, taken by an elevator to a chamber above the mill, from whence it descends to the millstones. After being finely ground it is spread out in the warehouse for a few days, when it is packed in casks or sacks for delivery.

'Portland cement is usually tested as to its tensile strength, and every English engineer who buys it applies his own tests, instead of adopting one general and fixed rule, as in Germany. At Folkestone the manager tests what strain the cement will bear after being kept for seven days under water. The test demanded by Mr. Brady at the Folkestone new harbour works is that it shall bear a strain of 810 lbs. on a sectional area of 2½ square inches seven days after moulding.'

During the process of grinding, samples are continually taken for the purpose of being tested. During the year 1881 the average of the tests at the Folkestone Works gave a tensile strength of 497 lbs. on the square inch of sectional area.

'The total output of Portland cement at the Folkestone Works is 120 tons per week.'



*Analysis of a Sample of Slurry taken from the Backs.*

The slurry dried at 100° C. contained :	
<i>Constituents insoluble in hydrochloric acid :</i>	
Silica . . . . .	14.956
Ferric oxide . . . . .	1.943
Alumina . . . . .	5.167
Lime . . . . .	.173
Water of combination and organic matter . . . . .	1.203
	<u>23.412</u>

*Constituents soluble in hydrochloric acid :*

Silica . . . . .	.230
Ferric oxide . . . . .	.493
Alumina . . . . .	.230
Carbonate of lime . . . . .	75.357
Magnesia . . . . .	.201
Sulphuric anhydride . . . . .	.057
Potash . . . . .	.070
Soda . . . . .	.127
	<u>76.765</u>

Constituents soluble in hydrochloric acid . 23.412 p.c.

Constituents insoluble in hydrochloric acid . 76.765

Total . 100.207

*Analysis of some Samples of Portland Cement.*

—	1	2	3	4	5
Insoluble residue . . . . .	1.260	2.566	2.894	4.909	1.674
Silica . . . . .	20.590	18.917	21.307	18.583	23.832
Alumina . . . . .	8.869	8.763	6.593	7.226	6.058
Ferric oxide . . . . .	4.998	4.412	5.386	5.108	3.127
Lime . . . . .	61.351	62.472	61.459	61.040	63.129
Magnesia . . . . .	.669	.841	.449	1.565	1.206
Sulphuric anhydride . . . . .	.886	.929	1.422	.763	.398
Potash . . . . .	.978	1.100	.437	.754	—
Soda . . . . .	—	—	.429	.271	—
	<u>100.000</u>	<u>100.000</u>	<u>100.376</u>	<u>100.219</u>	<u>99.424</u>

No. 1. The Folkestone Cement Company's, March, 1880.

No. 2. The Folkestone Cement Company's, September, 1881.

No. 3. From works on the Thames, 1881.

No. 4. A sample which possessed a strength of 500 lbs. on the square inch, made from a mixture of blue lias limestones.

No. 5 is especially interesting. The cement was made from refuse from the Channel Tunnel boring at the end of 1881, and possessed a high tensile strength.

‘Cement when thrown on to a sieve with 2,500 holes per square inch, should not leave more than 20 p.c. of residue.’

*Cement Manufacture, Cliff, Kent, Messrs. Francis & Co.—Table showing the percentage composition of the materials and products, and the changes due to burning, grinding, and mixing with water.*

—	Clay	Slurry	Cement	Gauged cement 7 days old carried 980 lbs.
Sand . . . . .	0.87	1.24	0.98	1.16
Silica . . . . .	54.14	11.77	20.45	18.77
Ferric oxide . . . . .	7.76	2.13	4.37	3.08
Alumina . . . . .	14.68	4.45	8.05	7.04
Magnesia . . . . .	—	—	1.48	1.52
Magnesium carbonate . . . . .	4.48	2.87	1.48	1.52
Lime . . . . .	—	—	62.13	54.89
Calcium sulphate . . . . .	—	—	2.13	1.73
“ carbonate . . . . .	2.01	69.97	—	—
Water and carbonic acid . . . . .	15.03	5.29	—	—
Water and organic matter . . . . .	—	—	—	9.45
	<u>98.97</u>	<u>97.72</u>	<u>101.07</u>	<u>98.96</u>

(The Engineer, vol. liii. p. 57, 1882.)

## CAUSE OF THE SETTING OF CEMENTS.

Cements which contain silica, lime, and alumina set and harden from the operation of other chemical reactions than those which can be given for the hardening and setting of mortar made of ‘fat’ lime and sand or plaster of Paris. In the first place, both the material and the conditions are different, and preclude the same causes from operation. The subject is one of great difficulty;

researches, some of an elaborate nature, carried on during the last hundred years, have not entirely satisfied our want of knowledge of the cause of the setting of cements, whether of natural or artificial origin. Fremy has arrived at the conclusion that calcium aluminate in hydrating becomes hard, and attributes the setting of cements chiefly to this cause. He also considers that pozzuolane consist essentially of

an alumina silicate which becomes hydrated, and which is then acted upon by calcium hydrate. It is this action which causes the setting, and not the hydration of the alumina silicate. Cements he considers to be mixtures of artificial pozzuolane with free lime. Feichtinger has also developed the view that the free lime in cements combines with the silicates and causes the setting and hardening. Schulatschenko criticises Frey's statement that pozzuolani and free lime constitute cements, and quotes Feichtinger, who shows that water decomposes the lime compounds in cements; and even the most dilute acids act in the same way. After washing Portland cement for fifteen days with hydrochloric acid diluted with 20 volumes of water, there remained nothing but pure silicates.

If Portland cement is mixed with a concentrated solution of ammonium carbonate, the greater part of the lime is converted into carbonate, and the mixture will not set. Remove the ammonium carbonate by washing, dry the cement, and mix it with water, still it will not set. If, however, some slaked lime be added, then the mixture sets. If the same cement be placed in water and subjected to a stream of carbon dioxide, the lime becomes carbonated, and the setting property of the cement is destroyed; it may, however, as in the previous case, be restored by the addition of a little slaked lime.

*The Researches of M. le Chatelier.*—In the *Annales des Mines*, February 1888, there is an account of long-continued work on this subject which may be said to be of an entirely novel character. When a thin section of a piece of Portland cement is examined in the microscope by the aid of polarised light, several crystalline substances are observed, together with a non-crystalline or amorphous matter. As these substances could not be separated mechanically so as to be submitted to chemical analysis, M. le Chatelier compared their optical properties with those of similar substances synthetically prepared.

The following is a description of the constituents of cement which present the most striking features:

1. *A substance which has no action on polarised light.* This is a calcium aluminate, rich in lime, and sometimes mixed with free lime. A tricalcic aluminate  $\text{Al}_2\text{O}_3 \cdot 3\text{CaO}$  has been obtained and found to be the only calcium compound besides lime itself which crystallises in the cubic system.

2. *A substance acting feebly on polarised light, and having a very distinct crystalline form.* This is a calcium silicate, considered to be the principal, if not the only, active constituent of cements; it is always the most important constituent, and sometimes cements are entirely composed of it. It is considered to be a calcareous peridotite  $2\text{CaO} \cdot \text{SiO}_2$ ; it crystallises in the substance 3 when cements are heated to fusion.

3. *A strongly coloured brown substance which acts upon polarised light.* It is the feeblest of the substances in cement; it constitutes the gangue of the substance 4, and in a state of fusion is the cause of its crystallisation. Its composition is that of a calcium aluminoferrite, poorer in lime than the tricalcic aluminate. Its composition

is  $2(\text{AlFe})_2\text{O}_3 \cdot 3\text{CaO}$ . It has been prepared directly and examined. It slowly alters in water, and undergoes but little change when it sets.

4. *Small crystals having a strong polarising action.* These are not abundant, and are of little importance, since they are unaltered by the action of water. They are supposed to be compounds of magnesia, for it has been proved that all the basic compounds of lime are altered by water, the contrary being the case with those of magnesia.

The effective constituents of cements are, first, the calcium ortho-silicate  $2\text{CaO} \cdot \text{SiO}_2$ ; secondly, one or more calcium aluminates and ferrites.

The action of water on cements causes the formation of several compounds; that which plays the chief part in the hardening process is a substance crystallising in hexagonal plates analogous to the crystals of calcium hydrate  $\text{CaH}_2\text{O}_2$ . No sufficient quantity has been obtained to make it possible to determine its composition. It is derived from the calcium ortho-silicate, and is much more abundant in cements which are entirely free from alumina. In quickly-setting aluminous cements long needles are found which interlace and are of considerable dimensions. In dry air they become dehydrated, and at  $50^\circ\text{C}$ . they fall to powder. They are the result of the action of water on the tricalcic aluminate. This substance  $\text{Al}_2\text{O}_3 \cdot 3\text{CaO}$  dissolves in pure water in the proportion of 3 decigrams per litre, and in salt water rather more freely, but with partial decomposition. These observations explain the practical differences between slowly and quickly-setting cements; the latter, always being highly aluminous, set as soon as the mass of interlaced hydrated crystals is formed, in a manner which is analogous to the setting of plaster of Paris (v. p. 471).

Besides these, Le Chatelier has discovered some other products of the reactions occurring in the setting of cements which do not act upon polarised light, but he has not been able to assign them any composition nor any part in the process of setting.

Calcium ortho-silicate,  $2\text{CaO} \cdot \text{SiO}_2$ , possesses a remarkable property, a knowledge of which serves to explain a phenomenon frequently observed in the manufacture of cements. Heated to fusion, it forms a semi-translucent stony mass, which, on being cooled slowly, disintegrates, and is finally reduced to an impalpable powder, consisting of minute twinned crystals. The unequal dilatation of the opposed faces of the twins is undoubtedly the cause of the disintegration. If the cement be not so strongly heated the twins are not formed, and the mass is not reduced to powder by cooling. There are certain minerals which, when heated, produce cements, such as *mouticellite*, a magnesian calcium silicate; this does not undergo these changes on heating and cooling. To sum up this work in a few words:

1. Cements contain, when of good quality, no free lime.

2. The constituents of cements are:

a. A tricalcic ortho-silicate  $3\text{CaO} \cdot \text{SiO}_2$ .

b. A tricalcic aluminate  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ .

c. A tricalcic aluminoferrite  $3\text{CaO} \cdot 2(\text{AlFe})_2\text{O}_3$ .

3. The calcium compounds, when the cement is tempered with water, are first decomposed, yielding calcium hydrate.

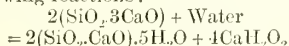
4. When the tricalcic compounds are decomposed, there are formed a hydrated crystalline ortho-calcic silicate and a hydrated calcium aluminate, while the calcium aluminoferrite, which slakes and swells like quicklime, is of little importance.

In some measure, a fact which is known to cement-makers corroborates Le Chatelier's views of the absence of free lime in cement. Good cement does not expand when set, whereas if an excess of lime be present, the cake of cement cracks in consequence of the expansion of free lime during slaking.

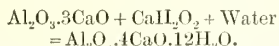
5. The setting is caused, as in the case of plaster of Paris, by the cement becoming a confused mass of crystals of the hydrated compounds mentioned.

6. The only hydrated calcium silicate obtained synthetically has the formula  $2(\text{CaO} \cdot \text{SiO}_2) \cdot 5\text{H}_2\text{O}$ . The only hydrated calcium aluminate which can exist in presence of an excess of lime has the composition  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ .

The formation of the hydrated silicate and aluminate in cement takes place according to the following reactions:



and



Between the *setting* and the *hardening* of cement there is no marked distinction as far as the chemical process is concerned; it will be

necessary to say merely that the setting is only the commencement of the hardening process. It is characterised by a progressive diminution in the fluidity of the mortar. The setting is complete when the nail makes no impression on the mass. In an aluminous cement the hydration of the aluminate will in great part cause the setting, and the hydration of the calcium silicate the hardening. The fineness of the powder and the porosity of the material will affect the progress of the hardening.

*Landrin's Researches.*—In ascertaining the properties of silica prepared in different ways it was found that insoluble silica, separated by acids from basic silicates and ignited at a low red heat, possessed the power of combining with lime and abstracting it from lime water. Gelatinous silica and soluble dialysed silica behave in like manner. The quantity taken up is 36 to 38 parts for 30 of silica, which corresponds with  $4\text{CaO} \cdot 3\text{SiO}_2$ . Such silica in a dry state, if mixed with lime, acts in the same manner as pozzuolane, and is referred to as *hydraulic silica*. Kieselguhr, if gently ignited, is hydraulic when mixed with lime. Pozzuolane owe their properties to the hydraulic silica they contain, and so likewise does the Theil lime.

If Theil lime be shaken with water free from carbonic acid, after a period of 12 or 15 days the soluble portion is found to contain (1) a large excess of lime capable of being carbonated; (2) soluble calcium aluminate; (3) alkaline silicates.

The composition of the insoluble residue is shown by Landrin to be a pozzuolana and a calcium aluminate, thus:—

#### *Analysis of Theil lime (Landrin).*

	Water and Carbonic acid	Silica	Ferric oxide and alumina	Lime	Magnesia	Total
Loss at a red heat . . .	4.40	—	—	—	—	4.40
Soluble in water . . .	—	4.70	1.05	35.10	0.36	41.21
Insoluble in water . . .	—	21.70	1.95	30.06	0.68	54.39
	4.40	26.40	3.0	65.16	1.04	100.0

Silica . . . 21.70	} Pozzuolana, or 'pozzo-portland'	48.58
Lime . . . 26.88		
Alumina & ferric oxide 1.95	} Calcium aluminate . . .	5.13
Lime . . . 3.18		
Magnesia . . . . .		0.68

Total as above	{ Insoluble . . .	51.39
	{ Soluble . . .	41.21
	{ Water and CO <sub>2</sub> . . .	4.40
		100.00

The Theil lime contains lumps which when calcined yield an excellent Portland cement; this property is attributed to the very large proportion of 'pozzo-portland' it contains. By heating to nearly a white heat, according to Landrin, mixtures of various silicas, even quartz, combine with lime. The mixture must be fritted but not fused; it then presents the following properties:

1. On cooling it falls to powder.
2. It entirely dissolves in hydrochloric acid.

3. Tempered with the smallest quantity of water it sets in 15 or 16 days, but never attains great hardness.

4. The hardness becomes comparable with that of the hardest stone if the water contains carbonic acid.

#### ON THE DETECTION OF ADULTERATIONS IN PORTLAND CEMENT.

R. Fresenius and W. Fresenius undertook a number of experiments at the request of the German Association of Cement Makers, on account of the increasing adulteration of cements. Numerous substances, such as ground shale, limestone, and other things, are readily detected, and therefore are not so often employed as formerly, but other substances of nearly the same composition as Portland cement have taken their place.

Experiments were made with 12 samples of pure Portland cement from different parts of Germany, England, and France, and these were compared with 3 kinds of hydraulic lime, 3 of



weathered slag-dust, and 2 of ground slag. The cements were of various ages and had been exposed to the air for different periods. There appeared to be, in many respects, a greater difference in the behaviour of the various pure Portland cements than between these and the adulterants, but the following determinations are sufficient to distinguish between them and to detect the presence of adulterants in Portland cement:

(a) The specific gravity.

(b) The loss on ignition.

(c) The alkalinity of water in which the substance has been placed.

(d) The action of dilute acid.

(e) The action of potassium permanganate.

(f) The action of gaseous carbon dioxide.

(a) For the specific gravity the method of Dr. Schumann was employed. The apparatus consists of a glass flask of 100 to 150 c.c. capacity, in the very short neck of which is placed, like a stopper, a tube of 40 c.c. capacity, graduated to  $\frac{1}{10}$ th c.c. The vessel is filled to the zero point with turpentine, and a weighed quantity of the solid is introduced gradually by means of a funnel. The weight divided by the increase of volume gives the specific gravity. The end of the graduated tube should be loosely corked to prevent evaporation, the temperature should be kept constant, and the vessel should be carefully shaken to remove all air from the solid. The specific gravity of pure Portland cement is never lower than 3.1, while that of the adulterant examined is always lower. The results were the same when the cement was very finely ground.

(b) About 2 grams were heated in a platinum crucible over a Bunsen burner for 20 minutes. The difference between Portland cement and hydraulic lime is very considerable.

(e) The substance was finely powdered and

passed through a sieve of 5,000 meshes to the square centimetre. One gram was shaken with 100 c.c. of distilled water at the ordinary temperature for 10 minutes. The solution was passed through a dry filter, and 50 c.c. was titrated with decinormal hydrochloric acid. The difference between cement and hydraulic lime is in this case considerable, that between the cement and the slag less so.

The results with lime are the highest, and with the slag lowest.

(d) One gram of the ground substance of the same fineness as in (c) was shaken with 30 c.c. of normal hydrochloric acid and 70 c.c. of water for 10 minutes; 50 c.c. of the filtrate were titrated with normal caustic soda. The results with the slag are considerably lower than with the other substances.

(c) The determination of the sulphur present in the form of metallic sulphides always came out lower in a mixture of cement and slag than when the two were analysed separately, because in the cement the iron was present as ferrie, and in the slag as ferrous oxide. The action of potassium permanganate was therefore studied. One gram of the substance finely powdered was treated with 150 c.c. of a mixture of 1 part of dilute sulphuric acid (sp.gr. 1.12) and 2 parts of water, and the solution was titrated with potassium permanganate.

The numbers with slag were much higher than with cement or lime, and were equally reliable with the slag alone or with a mixture of slag and cement. Hence the quantity of slag in the mixture can be determined.

(f) About 3 grams of the finely powdered substance (as in (c) and (d)) were placed in a weighed tube and subjected to the action of carbon dioxide, dried over sulphuric acid for about 2 hours, or until the weight became constant. The increase in weight gave the

Description	I. Specific gravity	II. Loss on ignition	III. Alkalinity of aqueous solution from 0.5 gr. in decinormal acid	IV. 1 gr. takes of normal acid	V. 1 gr. reduces of potassium permanganate	VI. 3 grs. absorb of carbonic anhydride
			c.c.	c.c.	mgr.	mgr.
Portland cement A	3.155	1.58	6.25	20.71	0.79	1.4
" " B	3.125	2.59	4.62	21.50	2.38	1.6
" " C	3.155	2.11	4.50	20.28	0.93	1.8
" " D	3.144	1.98	5.10	21.67	1.12	1.0
" " E	3.144	1.25	6.12	19.60	0.98	1.6
" " F	3.134	2.04	4.95	20.72	1.21	1.1
" " G	3.144	0.71	4.30	22.20	0.89	0.0
" " H	3.125	1.11	4.29	20.30	1.07	0.7
" " J	3.134	1.00	4.00	19.40	2.01	0.0
" " K	3.144	0.34	4.21	20.70	0.98	0.0
" " L	3.154	1.49	4.60	18.80	2.80	0.3
" " M	3.125	1.25	5.50	20.70	2.33	0.0
Hydraulic limo A	2.441	18.26	20.23	21.35	1.40	27.8
" " B	2.551	17.82	22.73	26.80	0.93	31.3
" " C	2.520	19.60	19.72	19.96	0.98	47.7
Weathered slag A	3.012	0.76	0.91	14.19	74.60	3.6
" " B	3.003	1.92	0.70	13.67	60.67	3.5
" " C	2.967	1.11	1.00	9.70	44.34	2.9
Ground slag I	3.003	0.32	0.31	3.60	64.40	2.4
" " II	2.873	0.43	0.11	8.20	73.27	2.2

amount of carbon dioxide absorbed. A small calcium-chloride tube was placed at the end of the weighed tube to absorb any water that might be evolved. The hydraulic lime was found to absorb by far the largest quantity of the gas.

The numbers in the case of a pure Portland cement should be as follows :

(a) Sp.gr. not lower than 3.1.

(b) Loss on ignition, between 0.3 and 2.59 p.c., certainly not much more.

(c) Alkalinity of an aqueous solution made from 0.5 grams of cement, corresponding to 4 c.c. or 6.25 c.c. of decinormal acid.

(d) Volume of normal acid neutralised by 1 gram of the powdered cement, 18.80 c.c. to 21.67 c.c., the lowest limit is not much below 18.8 c.c.

(e) Weight of permanganate reduced by 1 gram of cement, 0.79 to 2.8 milligrams, or not much more than 2.8.

(f) Weight of carbonic anhydride absorbed by 3 grams of cement 0 to 1.8 milligram.

The tests *a*, *c*, *d* and *e*, are applicable to the detection of slag, and *a*, *b*, *c* and *f*, to the detection of hydraulic lime.

Experimental mixtures of 9 parts of pure cement with one part of hydraulic lime, and with 1 part of slag respectively, showed that the adulteration could in every case be detected by this method of examination. It may be considered that the purity of a cement is proved if the numbers obtained on analysis fall within the limits quoted above (*Zeitschrift für analytische Chemie*, 23, 175; *Abstract J. Soc. Ch. Ind.* 3, 1881).

R. Weber, employing a magnifying power of 50.00 diameters, after adding acetic acid, found the cement particles to be clearly crystalline, whilst those of slag-powder were amorphous. The method, however, fails with particles which pass a sieve of 5,000 meshes per square centimetre. Dr. Heintzel proposes a fusion test for manganese as a means of detecting the admixture of slag-powder, since fine cement contains a minimum of manganese, whilst slag is comparatively rich in it.

**7. Oxychloride Cements.** In 1853 Sorel discovered the fact that zinc chloride mixed with zinc oxide united therewith to form a very hard cement. A solution of magnesium chloride in like manner sets with magnesia, the product being in both cases an oxychloride. The magnesium cement is of dazzling whiteness and great durability. It possesses the property of easily agglomerating sand in the proportions up to 20 parts for one of magnesia. The Union Stone Company of Boston, U.S., prepare magnesia by burning magnesite,  $MgCO_3$ , at a moderate temperature. When reduced to an impalpable powder, the magnesia is mixed with powdered marble or other similar material. The mixture is moistened with a solution of magnesium chloride of sp.gr. 1.162 to 1.263 in sufficient quantity to yield a plastic paste; this is pressed into moulds and left to harden, and at the end of 8 days it is fit for building purposes. Magnesium cement mixed with emery powder is used for making emery wheels and hones.

According to a recent patent, No. 7,304, May 6, 1881, fibrous asbestos is mixed with magnesia

and then saturated with a solution of magnesium chloride. It may be moulded into any form, but is especially applicable for use as boards or sheathing for roofings, wearing surfaces of car-brakes, and for building purposes.

**8. Artificial Stone.** The various substances classed under this description were all preceded by the material invented by F. Ransome, which was prepared from a paste of silicious sand or limestone with sodium silicate. The mass hardens, but is damaged by moisture unless the sodium salts are removed. The blocks are therefore steeped in a solution of calcium chloride whereby a calcium silicate is formed and sodium chloride is dissolved away. A modification of this process consisted in adding to a solution of an alkaline silicate, soluble silica obtained from near Farnham in Surrey, sand, and lime or materials containing lime. The ingredients are thoroughly mixed and placed in moulds. The insoluble calcium silicate is formed throughout the mass and in time a stone of great hardness is obtained. More recently it has been proposed by Ransome (Patent 6,517, April 18, 1884) to mix slag sand with caustic or slaked lime, or with spent oxide from gas-works, the sulphur in the latter being removed by a special process.

Artificial paving stones are made of sand and cement, or of coarsely powdered granite and cement. Similar mixtures have been used for the construction of water-cisterns in one piece, and crystallising tanks for chemical works.

Artificial lithographic stones, according to F. Wirth (Patent 3,808, February 23, 1884), may be prepared as follows:—

Cement is mixed and made to harden as quickly as possible, with warm water if necessary. This is allowed to form thin plates which are repeatedly moistened with water and heated till they shrink.

The plates are ground to powder and mixed with unset cement. The powder is compressed at 20 atmospheres in a mould, air is exhausted therefrom and water admitted, &c.

Stones thus produced are said to be superior to the natural Solenhofer stone.

**9. Concrete.** Concrete is an artificial stone composed of a mixture of sand, gravel, powdered granite, or sandstone with Portland or other cementing material, tempered so that the whole will set into a hard mass.

Mr. Bindon Stoney built the North Wall of the Liffey, at Dublin, of concrete blocks weighing no less than 330 tons apiece, and measuring 23 feet at the base, 26 feet deep, and 10 feet upon the face. They were built on a strong platform formed upon the shore to carry this enormous weight, and were allowed to remain long enough for them to harden before being removed. They were floated to their places and lowered to the base previously prepared for them under a large diving-bell 20 feet square. In fine weather they might be laid on an average of one block at every tide. Bridges and houses have been built without a joining, that is to say of one piece, with concrete; roads and streets have been made of it, and M. Coignet built 20 miles of sewers in Paris with it. Harbour works everywhere are more or less constructed of it.

A variety of concrete called *béton* is made in France. The difference between concrete and *béton* is this: while concrete is made by mixing dry cement and stones or gravel together and then adding water, *béton* is prepared by mixing a mortar of cement and sand, and the aggregate of gravel or other material. Concrete or *béton* may be prepared with the following cementing materials: (a) hydraulic lime, (b) hydraulic lime and trass, (c) hydraulic lime and pozzuolana, (d) Roman cement, (e) Portland cement.

Composition of different concretes:

Dublin, North Wall. Portland cement 1 part, Liffey gravel 10 parts.

Biarritz, Harbour of Refuge. Portland cement 1 part, sand 2 parts, broken stone 3 parts.

St. Jean de Luz. Portland cement 1 part, sand  $2\frac{1}{2}$  parts, stones 3 parts.

Trieste, quay walls. Santorin earth 7 measures, slaked lime 2 measures, broken stones 7 measures.

Trieste, quay walls. Santorin earth 14 measures, lime 5 measures, broken stones 12 measures.

Copenhagen, sea-forts. Portland cement 1 part, sand 4 parts, fragments of stones 16 parts.

The durability of concrete depends upon the excellence of the cement, the skill with which the concrete is mixed, and the suitability of the aggregate. Most disastrous accidents have happened through the decay of sea-walls and harbour works.

*The decay of cements.* The decay of cements exposed to sea-water appears in certain cases to have been due to the replacement of lime in the cement by magnesia derived from the salts in the sea-water. Magnesian cements, that is to say, Portland cements, containing a good deal of magnesia, have been recommended, but according to Lechartier such cements are not to be relied on, since they undergo a change in volume and disintegrate.

For harbour works engineers would do well not to approve of cements containing more than 1 p.c. of magnesia.

## II. Resinous Cements and Adhesive Materials.

The most important of the resinous cements are those termed *mastics*, which Vicat invented to supersede asphalt, a material which had been used in some of the most ancient structures.

The mastics are made of tar boiled with different materials such as lime or powdered brick. The composition which appears to have been of the most tenacious character was composed of 16 parts by weight of tar, and 36 parts of red brick cement. (Rapport sur un Mémoire de M. Vicat, intitulé Recherches sur les mastics résineux, A. 27, 79.)

Lime boiled in tar is used to cement stones such as Yorkshire flags, for the purpose of rendering them air-tight to corrosive gases in the construction of absorbing towers and acid tanks in chemical works.

Unlike plaster of Paris and hydraulic cements, which are more or less crystalline when set, most other adhesive materials are colloid substances and may be divided into three classes.

## I. Resinous Cements.

1. Those which soften by heat and harden when cold: *sealing wax*; *marine glue*.

2. Those which are dissolved but which harden by evaporation of the solvent. The solvent may be either a hydrocarbon or a hydrocarbon derivative as alcohol or chloroform. *Caoutchouc in chloroform*; *Canada balsam*; *Dammor resin*; *Balsams*, that is to say resins found in solution in hydrocarbons of the terpene class.

## II. Oleaginous Cements.

3. Mixtures containing oils which harden by oxidation when exposed to the air. *White lead*; *Red lead*; *Putty*.

## III. Gummy and Gelatinous Cements.

4. Those which do not soften by heat but soften in water. *Gum arabic*; *Dextrin*; *Gelatine*; *Glue*.

5. Those which are either gelatinised or dissolved in water, or in some aqueous solution, and harden by absorption of the water by the materials cemented. *Starch paste*; *Gelatine in water*; *Liquid glue*; *Gelatine in acetic acid*; *Albumen*; *Albumen and lime*.

Gum, glue, and paste are cements, the uses of which are well known.

Diamond cement is a preparation of isinglass and gum ammoniacum dissolved in alcohol (*v. GUM RESINS*). It is employed to mend glass and china.

Sir John Robinson's cement is thus described:

'If it be wished to dissolve good isinglass in spirits of wine, it should first be allowed to soak for some time in cold water. When swelled it is to be put into the spirit, and the bottle containing it being set in a pan of cold water may be brought to the boiling point, when the isinglass will melt into a uniform jelly, without lumps or strings, which it is apt to have when not swelled in cold water previously to being put into spirits. A small addition of any essential oil diminishes its tendency to become mouldy.

'If gelatine which has been swelled in cold water be immersed in linseed oil and heated it dissolves, and forms a glue of remarkable tenacity, which, when once dry, perfectly resists damp, and two pieces of wood joined by it will separate anywhere else rather than at the joint. Ordinary glue may be thus dissolved, and sometimes a small quantity of red lead in powder is added.'

Shellac dissolved in alcohol, or in a solution of borax, or still better in naphtha, forms a good cement. White of egg alone, or mixed with finely sifted quicklime, will answer for uniting objects which are not exposed to moisture. The latter combination is very strong, and is much employed for joining pieces of spar and marble ornaments. A similar composition is used by copper-smiths to secure the edges and rivets of boilers, only bullock's blood is the albuminous matter used instead of white of egg. Another cement in which an analogous substance, the curd or casein of milk, is employed, is made by boiling slices of skim-milk cheeses into a gluey consistence in a great quantity of water, and then incorporating the mixture with quicklime



on a slab with a muller, or in a marble mortar. When this compound is applied warm to broken edges of stoneware, it unites them very firmly after it is cold.

A cement which gradually indurates to a stony consistence may be made by mixing 20 parts of clean river sand, 2 of litharge, and 1 of quicklime, into a thin putty with linseed oil. When this cement is applied to mend broken pieces of stone, as steps of stairs, it acquires after some time a stony hardness.

The iron-rust cement is made of from 50 to 100 parts of iron borings, pounded and sifted, mixed with 1 part of sal ammoniac, and when it is to be applied, moistened with as much water as will give it a pasty consistency. Formerly flowers of sulphur were used, and much more sal ammoniac, in making this cement, but with decided disadvantage, as the union is affected by the oxidation, and consequent expansion and solidification of the iron powder, and any heterogeneous matter obstructs the effect. The best proportion of sal ammoniac is 1 p.c. of the iron borings. Another composition of the same kind is made by mixing 4 parts of fine borings or filings of iron, 2 parts of potter's clay, and 1 part of pounded potsherds, and making them into a paste with salt and water. When this cement is allowed to concrete slowly on iron joints it becomes very hard.

For making architectural ornaments in relief, a moulding composition is formed of chalk, glue, and paper paste. Even statues have been made with it, the paper aiding the cohesion of the mass. Some French statuettes are so made.

Mastics of a resinous or bituminous nature which must be softened or fused by heat are the following.

Varley's cement consists of 16 parts of whiting sifted and thoroughly dried by a red heat, adding when cold a melted mixture of 16 parts of black resin and 1 of beeswax, and stirring well during the cooling.

Singer's cement for electrical and chemical apparatus consists of 5 lbs. of resin, 1 of beeswax, 1 of red ochre, and 2 tablespoonfuls of Paris-plaster, all melted together. The ochre and the plaster of Paris should be calcined beforehand, and added to the other ingredients in their melted state. The thinner the stratum of cement that is interposed, the stronger, generally speaking, is the junction.

Boiled linseed oil and red lead mixed together into a putty are often used by copper-smiths and engineers to secure joints. The washers of leather or cloth are smeared with this mixture in a pasty state.

The resin mastic is sometimes used by jewellers to cement cameos of white enamel or coloured glass to a real stone, as a ground to produce the appearance of an onyx. Mastic is likewise used to cement false backs or doublets to stones to alter their hue.

Melted brimstone, either alone or mixed with resin and brickdust, forms a tolerably good and very cheap cement.

Plumber's cement consists of black resin 1 part, brickdust 2 parts, well incorporated by a melting heat.

The cement for coating the fronts of buildings consists of linseed oil boiled with litharge, and

mixed with porcelain clay in fine powder, to give it the consistence of stiff mortar. Pipe-clay would answer equally well if well dried, and any colour might be given with ground bricks or pottery. A little oil of turpentine to thin this cement aids its cohesion upon stone, brick, or wood. It has been applied to sheets of wire cloth, and in this state laid upon terraces, in order to make them water-tight; but it is little less expensive than lead.

The bituminous or black cement for bottle corks consists of pitch hardened by the addition of resin and brickdust.

In certain localities where a limestone impregnated with bitumen occurs, it is dried, ground, sifted, and then mixed with about its own weight of melted pitch. When this mixture is getting semi-fluid, it may be moulded into large slabs or tiles in wooden frames lined with sheet-iron, previously smeared over with common lime mortar, in order to prevent adhesion to the moulds, which, being in movable pieces, are easily dismounted so as to turn out the cake of artificial bituminous stone. This cement is manufactured upon a great scale in many places, and used for making Italian terraces, covering the floors of balconies, flat roofs, water reservoirs, water conduits, &c. When laid down, the joints must be well run together with hot irons. The floor of the terrace should be previously covered with a layer of Paris plaster, or common mortar, nearly an inch thick, with a regular slope of one inch to the yard. Such bituminous cement weighs 144 pounds the cubic foot; or a foot of square surface, one inch thick, weighs 12 lbs. Sometimes a second layer of these slabs or tiles is applied over the first, with the precaution of making the seams or joints of the upper correspond with the middle of the under ones. Occasionally a bottom bed, of coarse cloth or grey paper, is applied.

An excellent cement for resisting moisture is made by incorporating thoroughly 8 parts of melted glue, of the consistence used by carpenters, with 4 parts of linseed oil, boiled into varnish with litharge. This cement hardens in about forty-eight hours, and renders the joints of wooden cisterns and casks air and water tight. A compound of glue with one-fourth its weight of Venice turpentine, made as above, serves to cement glass, metal, and wood to one another. The gluten of wheat, well prepared, is also a good cement. White of eggs with flour and water well mixed, and smeared over linen cloth, forms a ready lute for steam joints in small apparatus.

White lead ground upon a slab, with linseed oil varnish, and kept out of contact of air, affords a cement capable of repairing fractured articles of all kinds. It requires a few weeks to harden. When stone and iron are to be cemented together, a compound of equal parts of sulphur and pitch answers very well.

Lapidaries' cement is made of resin, tempered with beeswax and a little tallow, and hardened with red ochre or Spanish brown and whiting.

Opticians' cement, for fixing glasses for grinding, is made by mixing sifted wood ashes with melted pitch; the ashes absorb the oil in the pitch, and the adhesiveness of the pitch is thereby reduced. The proportions are some-

what varied with the temperature of the season and the qualities of the pitch; but generally about 4 lbs. of wood ashes to 14 lbs. of pitch are employed, and the cement, if too hard and brittle, is softened with hog's lard and tallow.

Japanese cement is said to be prepared by intimately mixing rice flour with cold water, and then boiling the mixture; it is white, and dries nearly transparent.

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## CERADIA v. OLEO-RESINS.

## CERASIN v. GUMS.

**CERASINE.** Syn. *Fast Red, Roccellin, Orseille* 4, *Rubidine*, v. AZO-COLOURING MATTERS.

**CERASINOSE**  $C_6H_{12}O_6$  or  $C_5H_{10}O_3$  obtained by Sachsse and Martin by the action of sulphuric acid on cherry-tree gum. It is converted by acids, and long standing in solution, into arabinose (Martin and Sachsse, *Phytochemische Untersuchungen*, Leipzig, 1880). The body is probably a mixture of arabinose and galactose (O'S. & H.).

**CEREALS.** The grain-bearing plants of which a brief account will be given in this article, are wheat, oats, barley, maize, rice, and millet. We shall consider: 1. The proximate composition of the harvested grain and straw, their parts and products; with some reference to the influence of climate, season, and manuring on this composition. 2. The composition of the ash, with the alterations due to season and manuring. We shall conclude with a brief reference to the chemical life-history of these crops, and the amount of plant food which they remove from the soil.

**I. Proximate composition. 1. Whole grain.** The following table shows the average composition, as far as at present ascertained, of the

various cereal grains. As climate has a considerable influence on the character of a seed, the composition of the grain of different countries has been given separately in some cases, when sufficient material existed for such a statement. The analyses marked 'König' are taken from his 'Chemische Zusammensetzung der menschlichen Nahrungs- und Genussmittel,' 1882, supplemented in some cases by later analyses published in the Jahresbericht. Those marked 'Richardson' from Am. 6, 302; or from Bulletin No. 9, Department of Agriculture, Washington, 1886. Those marked 'Johnson' from Report of Connecticut Agricultural Station, 1884. Those marked 'Church,' are from his Food Grains of India, 1886.

In calculating the ratio of nitrogenous to non-nitrogenous substance, it is assumed that the fibre is undigested by man. The fat is multiplied by 2.5 and added to the carbohydrates, the sum giving the total non-nitrogenous substance in the food reckoned as starch. This total is then divided by the amount of nitrogenous substance. The ratios would probably be wider if we could take into account the relative proportions of nitrogenous and non-nitrogenous matter digested by man.

Average Composition of Cereal Grains.

—	Number of analyses	Water	Nitrogenous substance	Fat	Carbo-hydrates	Fibre	Ash	Authorities	Ratio of nitrogenous to non-nitrogenous substance
Wheat (European, excluding Russian) . . . . .	208	13.7	12.3	1.8	67.9	2.5	1.8	{ König (chiefly)	1:5.9
" (American) mean . . . . .	407	10.2	12.2	2.2	71.7	1.8	1.9	Richardson	1:6.3
" " highest p.e. . . . .	—	12.5	18.0	3.6	78.7	3.1	3.6	"	—
" " lowest p.e. . . . .	—	7.7	7.7	1.4	64.8	0.4	0.8	"	—
" (East Indian) . . . . .	—	12.5	13.5	1.2	68.1	2.7	1.7	Church	1:5.3
Spelt, with husk . . . . .	12	12.1	11.0	2.8	66.4	5.5	2.2	König	1:6.7
Rye (European) . . . . .	43	15.0	11.5	1.8	67.9	2.0	1.8	König	1:6.3
" (American) mean . . . . .	57	8.7	11.3	1.9	74.5	1.5	2.1	Richardson	1:7.0
" " highest p.e. . . . .	—	10.0	15.6	2.9	77.5	1.9	3.7	"	—
" " lowest p.e. . . . .	—	7.0	8.3	1.1	68.7	1.1	1.3	"	—
Oats, with husk (European) . . . . .	170	12.3	10.4	5.2	58.0	11.1	3.0	{ König (chiefly)	1:6.8
" (American) mean . . . . .	1007	6.1	10.8	5.9	67.4	6.3	3.2	Richardson	1:7.6
" without husk . . . . .	179	6.9	14.3	8.1	67.1	1.4	2.2	"	1:6.1
" " highest p.e. . . . .	—	11.1	19.1	11.2	71.9	2.1	2.9	"	—
" " lowest p.e. . . . .	—	4.7	9.1	6.5	62.8	0.9	0.9	"	—
Barley (European) . . . . .	125	13.7	11.1	2.2	65.0	5.3	2.7	König	1:6.4
" (Saxon) . . . . .	many	15.0	8.4	1.6	66.8	4.6	3.6	Mareker	1:8.1
" (Canadian) . . . . .	12	8.0	9.8	2.7	73.2	3.5	2.8	Richardson	1:8.2
" (United States) mean . . . . .	60	6.5	11.3	2.7	72.8	3.8	2.9	"	1:7.0
" " highest p.e. . . . .	—	9.2	14.9	3.5	76.8	4.7	4.1	"	—
" " lowest p.e. . . . .	—	4.5	8.8	2.1	63.0	2.6	1.5	"	—
" without husk (United States) . . . . .	15	6.3	11.8	2.7	75.1	1.6	2.2	"	1:7.0
Maize (European) . . . . .	27	13.3	9.8	4.5	68.4	2.5	1.5	König	1:8.1
" (American) mean . . . . .	111	10.0	10.5	5.2	70.7	2.1	1.5	Richardson	1:8.0
" " highest p.e. . . . .	—	15.1	13.7	7.5	75.7	3.1	3.1	"	—
" " lowest p.e. . . . .	—	7.4	7.0	3.9	66.0	0.8	1.0	"	—
Rice with husk . . . . .	1	9.6	5.9	1.8	72.7	5.8	4.2	König	1:13.1
" cleaned (American) . . . . .	10	12.4	7.1	0.4	79.2	0.2	0.4	Johnson	1:10.8
" " (East Indian) . . . . .	—	12.8	7.3	0.6	78.3	0.4	0.6	Church	1:10.9
" " (Japanese) . . . . .	—	12.8	6.1	2.0	73.9	4.0	1.2	König	1:12.9
Millet, <i>Sorghum vulgare</i> . . . . .	—	12.5	9.3	2.0	72.3	2.2	1.7	Church	1:8.3
" <i>farfarcum</i> . . . . .	7	11.1	9.5	4.2	71.7	1.7	1.3	various	1:8.2
" <i>Panicum miliaceum</i> with husk . . . . .	2	13.2	10.2	3.8	56.9	12.8	3.1	"	1:6.5
" " without husk . . . . .	6	11.6	12.4	4.7	65.6	3.3	2.4	{ König (chiefly)	1:6.2
" " <i>miliare</i> . . . . .	—	10.2	9.1	3.6	69.0	4.6	3.5	Church	1:8.6
" " <i>frumentaceum</i> . . . . .	—	12.0	8.4	3.0	72.5	2.2	1.9	Church	1:9.5
" " <i>colonum</i> without husk . . . . .	—	12.0	9.6	0.6	74.3	1.5	2.0	Church	1:7.9
" <i>Paspalum scrobiculatum</i> with husk . . . . .	—	11.7	7.0	2.1	77.2	0.7	1.3	Church	1:11.8
" <i>Panicum hypochaerium</i> with husk . . . . .	—	11.3	10.4	3.3	71.5	1.5	2.0	Church	1:7.7
" <i>Setaria italica</i> without husk . . . . .	—	10.2	10.8	2.0	73.4	1.5	1.2	Church	1:7.5
" <i>Elysinus coracum</i> with husk . . . . .	—	12.5	5.9	0.8	74.6	3.6	2.6	Church	1:13.0
" " without husk . . . . .	—	13.2	7.3	1.5	73.2	2.5	2.3	Church	1:10.6

The cereal grains containing, for an equal weight, the largest supply of nutriment, are oats (deprived of husk) and maize; some of the millets that are rich in fat may equal maize, but the average composition of the millets is at present imperfectly ascertained. The grains richest in nitrogenous substance are the kernel of oats, and the wheat of hot dry climates, notably that of South Russia. Some analyses of the kernel of *P. miliaceum* also show 14.15 p.c. of nitrogenous substance. The relation of nitrogenous to non-nitrogenous substance is seen from the table to vary from 1 : 5.3 in the case of Indian wheat, to 1 : 10.9 in the case of cleaned rice, and to even a wider ratio in the case of some of the millets. The grains richest in fat are oats and maize; a few of the millets perhaps equal maize. The notable proportion of fat in oats and maize is of considerable importance, as fat is a constituent generally deficient in cereal grains. Cleaned rice is pre-eminent among the cereals for its high proportion of starch, and low proportion of ash. It is of little use to compare the percentage of ash found in different grains, as any seed having a thick husk or bran will yield more ash than one not so covered; for dietetic purposes we should compare, not the seeds, but the flour or meal prepared from them.

Most cereal grains exhibit a wide range of composition, depending on 1. the variety of the species; 2. the character of the soil; 3. the conditions of the season when grown: this last condition is perhaps the most important. Cereals having a thick husk (as oats), vary greatly in composition according to the proportion of husk to kernel; with such grains the higher the weight per bushel, the larger will be the proportion of kernel. An abundant supply of nitrogenous food in the soil, especially if the most essential ash constituents, phosphoric acid and potash, are deficient, will tend to increase the proportion of nitrogenous substance in the grain. The supply of nitrogen and ash constituents from the soil is comparatively little affected by season, but the assimilation of carbon from the atmosphere by the crop is directly dependent on the length of the period of growth, and on the conditions of light, heat, and moisture during that period. Premature or imperfect ripening thus implies a deficiency of starch in the grain, and consequently a high proportion of nitrogenous substance. With the same food supply from the soil, and a longer or more favourable season for growth, the yield of grain will be much more considerable, and the proportion of starch it contains much greater. Wheat exhibits an extraordinary variation in its percentage of nitrogenous substance. Shrivelled grains are more nitrogenous than plump ones from the same crop. Spring-sown wheat, having a shorter period of growth, is generally more nitrogenous than autumn sown wheat. The largest proportion of nitrogen is reached when the soil is rich, and the climate hot and dry, bringing about a premature ripening; the crop is then small, but the grain highly nitrogenous. Such is the case in South Russia, and in parts of India. Laskowsky (A. 135, 346) found in South Russian wheat 21.56 p.c. of nitrogenous substance, as a mean of 21 analyses:

the maximum was 24.16 p.c. Millon, Péligot, v. Bibra, and Ritthausen have also found abnormally high percentages of nitrogen in this wheat. The barley of South Russia is also remarkable for its high nitrogen. Wheat grain is distinguished as hard or soft, according to its clear and horny or opaque and mealy character. In grains from the same source the clear will always be found more nitrogenous than the mealy (Church). Hard wheat is generally more nitrogenous than soft wheat, but soft wheat is not necessarily poor in nitrogen. Illustrations, from the experiments of Lawes and Gilbert, of the variation in the nitrogen of wheat grain and straw grown in different seasons and by different manures, will be found in the tables on page 498.

While wheat furnishes the best example of the conditions which produce a nitrogenous grain, the cultivation of fine malting barley excellently illustrates the conditions necessary for the production of a grain rich in starch. Fine malting barley should contain but 8.9 p.c. of nitrogenous substance; such grain can only be produced in temperate climates, and on soil supplying only a moderate amount of nitrogenous food. The barley of highly manured soil, or of climates too hot or too cold, will fail to contain the large proportion of starch desired.

The amount of nitrogenous substance in the cereal grains given in the table is obtained by multiplying the nitrogen by 6.25; in the analyses given by Church, the multiplier is 6.3. The nitrogen is thus reckoned as present in the form of albuminoids. A small part of the nitrogen is, however, not albuminoid, but exists probably as amides. But few determinations have yet been made on the proportion of true albuminoids in cereal grains, and the analyses have been made with different, and in some cases imperfect methods. The mean proportion of albuminoid nitrogen found for 100 of total nitrogen has been as follows:

Wheat (6 analyses) . . .	90.1 p.c.
Rye (1 analysis) . . .	77.1 "
Oats (28 analyses) . . .	94.3 "
Barley (7 analyses) . . .	94.3 "
Maize (4 analyses) . . .	87.3 "
Rice (1 analysis) . . .	91.7 "
Millet, <i>P. italicum</i> (1 an.) . .	90.0 "
" <i>P. miliaceum</i> (1 an.) . .	96.7 "
" <i>S. saccharatum</i> (1 an.) . .	88.0 "
" <i>S. tartaricum</i> (1 an.) . .	90.7 "

Rye, maize, wheat, and some of the millets, thus appear to stand below oats and barley as to the proportion of nitrogen existing as albuminoids. In the case of rye and wheat this is doubtless due to the low proportion of albuminoids existing in the bran of those grains. Grain which has been damaged by damp, and partially germinated, contains a smaller proportion of albuminoid, and a larger proportion of amide nitrogen than sound grain. Thus malt, mean of six analyses, contains only 79.2 p.c. of its total nitrogen as albuminoids.

The flour of wheat and spelt yields the well known gluten when kneaded in a stream of water. According to Bénéard and Girardin (J. Ph. [5] 4, 127), the paste should not be washed for at least three hours, as the quantity of gluten increases on standing. Frear (Am. 6, 402) found

a great increase during the first 30 minutes, but a tendency to decrease after 45 minutes or one hour. According to Sidney Martin no gluten is obtained if the flour is kneaded with water at the temperature of 2°; the most favourable temperature is about 30°. The flour also yields little gluten if treated at first with a large quantity of water. If the albuminoids of the flour have been coagulated by long heating at 60°, no gluten is obtainable. The quantity of gluten generally rises and falls with the total nitrogen in the flour, but without much regularity. Ritthausen obtained from 33 flours, having a wide range of composition, from 7.08-18.54 p.e. of pure gluten. He found that an average of 78.3 p.e. (extremes 88.67 p.e.) of the nitrogen of the flour was found in the gluten. The gluten of soft wheats is friable and not fitted to produce an elastic dough; the gluten of hard wheat is far more tenacious.

The nature of the albuminoids in cereal grains has been carefully studied by Ritthausen and Kreuzler (*Die Eiweisskörper der Getreidearten, Hülsenfrüchte, und Oelsamen*, 1872). The method was to extract the meal with water, with spirit, and finally with a highly dilute solution of potassium hydrate. From wheat gluten, spirit extracted albuminoids which Ritthausen named *gluten-fibrin*, *gliadin* (Glutin, Pflanzenleim), and *mucedin*. The portion insoluble in spirit yielded to potash water *gluten-casein* (Pflanzenfibrin, Zymon). To gliadin the elastic character of gluten is attributed; it was found most abundantly in hard wheat. Rye yielded mucedin and gluten-casein. Oats yielded principally *oat-legumin* (Pflanzen-Casein, Avenine), and a small quantity of *oat-gliadin*. Barley, gluten-casein, gluten-fibrin, and mucedin. Maize, *maize-fibrin* (Zein), and a body similar to conglutin. Albumin was more or less certainly indicated in most of the cereals.

The investigation of the albuminoids has been conducted by methods differing from those employed by Ritthausen, and with entirely different results, by Denis, Weyl, Vines, Martin, and others. That the gluten of wheat does not consist of a substance originally present in the flour, but has been formed from the albuminoids of the grain by the action of water, is certainly indicated by the facts relating to the production of gluten already stated; it is further confirmed by the action of a 10-15 p.e. solution of sodium chloride, which extracts freely the albuminoids of the flour, but is without effect on gluten. Alcohol of 80 p.e., again, extracts no albuminoids from wheat flour, unless it has previously been treated with water (Martin), but dissolves a considerable amount from gluten. Weyl concludes that gluten is formed by a ferment, the action being started by the presence of water.

The investigators just named all conclude that *globulin* is a chief constituent of the albuminoids of seeds; the caseins obtained by Ritthausen are regarded as globulin changed into albuminate by the action of dilute alkalis or acids. According to Martin, wheat, rye, and barley all contain a globulin of the myosin type, insoluble in water, but soluble in a 10-15 p.e. sodium chloride solution, from which it is precipitated by heat (even at 35°-40° if long con-

tinued), or by saturation with sodium chloride. These cereals also contain an *albumose*, soluble in water, and not precipitated on boiling. For the full reaction of these bodies we must refer to Martin's original papers. The gluten produced by the action of water on wheat flour consists of insoluble albumose and gluten-fibrin; the former is soluble in 80 p.e. alcohol, and comprises the gliadin, mucedin, and gluten-fibrin of Ritthausen. The insoluble albumose has apparently been derived from the soluble albumose of the flour, and the gluten fibrin from the globulin. The principal papers on the subject are by Weyl (H. 1, 72; B. 13, 367), Vines (Ph. 3, 93), Martin (P. Ph. S. Feb. 2, 1887; B. M. J. 2, 1886, 101).

The conclusions thus arrived at respecting the formation of gluten have recently been traversed by Johannsen (Compt. rend. Laboratoire de Carlsberg, 1888, 199). He prepared an artificial flour from gluten and starch, and found that it behaved as regards temperature, and the action of salt and metallic solutions, precisely as a natural flour. He concludes therefore that the ferment theory of the formation of gluten is superfluous.

*Nuclein* must probably be included among the nitrogenous bodies present in cereal grains; no determinations of its quantity have apparently been made.

The fats contained in the cereal grains are as yet but imperfectly investigated. According to J. König (*Nahrungsmittel*, 325), their elementary composition is as follows:—

—	C	H	O
Wheat (fluid) .	77.19	11.97	10.84
Rye " .	76.71	11.79	11.50
Barley (solid) .	76.29	11.76	11.95
Oats (fluid) .	75.71	11.68	12.61
Maize " .	75.70	11.35	12.95

The fat of rye contains, according to König, *oleic*, *palmitic*, and *stearic* acids, a part of which is apparently in the free state. Ritthausen did not find stearic acid. He found a little cholesterol both in rye and wheat. In maize oil, Allemann found the three acids already named.

The immature grains of wheat, rye, oats, and barley contain, according to Müntz (*Annales de la Science Agronomique*, 1884, 8), a large amount of *synanthrose*, which as ripening progresses is replaced by starch. Thus 100 parts of dry rye grain contained:

—	Synanthrose	Starch
10 days after blooming	45.0	24.6
19 " "	30.5	37.7
29 " "	19.1	47.4
41 " "	15.3	56.8
53 " "	13.1	64.0
59 " "	6.9	68.8

The last date was the time of harvest. The synanthrose apparently continues to decrease after the grain is harvested. The proportion in rye bran (4.2 p.e.) is greater than in the white flour (2.3 p.e.). In wheat, oats, and barley synanthrose was found in large quantity in the



unripe grain, but none in that fully matured. In unripe maize, fruit-sugar (equal parts dextrose and levulose) was found in place of synanthrose. Unripe wheat and barley contains, according to Müntz, a ferment, which, when the grain is bruised, slowly converts synanthrose (and sucrose) into dextrose and levulose.

The carbohydrates of the cereal grains have been the subject of numerous investigations; the conclusions arrived at have not unfrequently been inaccurate, the investigator too often relying on qualitative reactions for the purpose of identification. Certainty in this difficult branch of investigation can only be attained when the carbohydrate has been separated in a pure state, and its optical properties, and the products of its hydrolysis, have been determined.

In the ripe grain of cereals starch forms by far the largest constituent. In most published analyses its proportion is overstated, being calculated from the glucose obtained on boiling with acid. The only accurate method for determining starch is by treatment with pure diastase, and estimation of the maltose and dextrin produced (C. J. 45, 1). O'Sullivan found by this method 55.4 p.c. starch in white wheat; 44.46 p.c. in rye; 35.38 p.c. in white oats; 39.57 p.c. in barley; 54.58 p.c. in yellow maize; 75.77 p.c. in rice.

The starch contained in the glutinous rice of Siam is, according to Kreusler and Dafert (A. a. 11, 478), coloured red-brown by iodine. This rice contains a considerable amount of sugar, 8.65 p.c. of the dry substance.

*Dextrin* appears in many analyses among the minor constituents of cereal grains. It has been usual to designate thus any carbohydrate soluble in water, insoluble in alcohol, and reducing copper only after boiling with acids. The presence of dextrin in ungerminated grain cannot yet be considered as established.

*Amylan* is the name given by O'Sullivan to two gummy bodies of little solubility, having the percentage and composition of starch. Barley contains 2.4 p.c., chiefly of the less soluble  $\alpha$ -amylan; wheat and rye 2.25 p.c. of  $\beta$ -amylan and 0.5-1.0 p.c. of  $\alpha$ -amylan (C. J. 41, 21). The *sinistrin* found by Kühnemann in barley (B. 8, 389) is possibly identical with anylan.

*Gum* is mentioned in many analyses of cereals. Müntz, for instance, in the paper referred to above, and again in C. R. 102, 681, speaks of gum as occurring in wheat, rye, and barley, especially in the last two, in which the amount is given as 2.3 and 2.8 p.c. Until, however, the substance in question is isolated and fully examined, the actual existence of arabic acid can hardly be considered as proved.

The presence of *sucrose* in cereal grains may be taken as fully established. O'Sullivan found 0.8-1.6 p.c. in barley, and in wheat 0.5 p.c. (C. J. 49, 64); other chemists have recognised the same sugar in oats and maize. During germination the proportion of sucrose in barley is considerably increased. Besides sucrose, other sugars, both dextrorotatory and levorotatory, are apparently present in ripe grain, but have not yet been accurately discriminated.

*Raffinose* has been found by O'Sullivan in barley (C. J. 49, 70).

There is apparently a considerable amount of unidentified carbohydrates in cereal grains. Richardson found the total quantities of carbohydrates soluble in cold water in the various cereals to be on an average—for rye 12.3 p.c., barley 10.6 p.c., oats 9.5 p.c., wheat 5.8 p.c., and maize 4.4 p.c. Rye thus appears especially rich in soluble carbohydrates; according to Ritt-hausen it contains mucilage.

The total *pectic* bodies (pectose, pectine, and pectates) occurring in cereal grains have been determined by Schloesing's method by several French chemists. Müntz (C. R. 102, 624, 681; Ann. de l'Institut nat. agron. 2, 88) found in barley 0.9 p.c., in rye 0.7 p.c., in wheat 0.5 p.c., in oats 0.4 p.c., in maize 0.2 p.c. Müntz regards the presence of pectic bodies and of gum in feeding stuffs as of considerable physiological interest, as these bodies yield galactose among the products of their hydrolysis, and he supposes that sugar of milk is formed in the animal by the union of glucose and galactose, which are the products which sugar of milk yields on hydrolysis.

The amount of *cellulose* present in cereal grains is greatly underrated in ordinary analyses. The 'fibre' mentioned in the table on p. 490 is merely the residue left after boiling with dilute acid and alkali, a treatment which converts a considerable portion of the cellulose into glucose. Müntz, by dissolving out the cellulose with Schweitzer's copper reagent, reprecipitating with acid, and weighing, obtained from oats 15.5 p.c. of cellulose, and from maize 2.7 p.c., while the ordinary determinations of fibre gave respectively 9.80 and 1.94 p.c. The fibre contained a higher percentage of carbon than is proper to cellulose, thus indicating the presence of *lignose*.

The composition of wheat grain in different stages of growth has been ascertained by Heinrich (Wolff's Aschen Analysen, 1880, 1).

2. *The parts and products of cereal grains.* The relative composition of the parts of cereal grains is readily understood if we bear in mind a few facts relating to their structure. The chaff surrounding the seed in all cases consists very largely of woody fibre, it yields a considerable amount of silicious ash, and contains a very small proportion of nitrogen; it is, in fact, similar to straw in its composition. With some seeds, as oats and barley, the chaff is adherent to the grain, and consequently forms part of the milling products; in other seeds, as wheat and rye, the chaff is not adherent, and is absent from the milling products. The seed, free from chaff, may be divided according to chemical composition into four main portions.

(1) External fibrous layers, characterised by a considerable proportion of woody fibre and ash, and more or less rich in fatty matters and nitrogen.

(2) A layer beneath these, especially rich in albuminoid substances.

(3) The endosperm, forming the bulk of the grain; this in cereals is extremely rich in starch, contains a very small proportion both of ash constituents and fat, and is generally poor in nitrogen.

(4) The embryo; this far exceeds all the other parts of the grain in its contents of nitrogenous matter and fat.

In the table below the average composition is given of some of the principal parts and products obtained from cereal grains. The analyses marked 'Wolff' are from Mentzel u. Lengerke's

Kalender, 1888. Those marked 'Johnson' are from the Report of the Connecticut Agricultural Station for 1888. References to the other authorities have been already given.

*Parts and Products of Cereal Grains.*

—	Number of analyses	Water	Nitrogenous substance	Fat	Carbo-hydrates	Fibre	Ash	Authorities
Wheat flour, finest . . .	10	13.3	10.2	0.9	74.8	0.3	0.5	König
" " coarsest . . .	27	12.7	11.8	1.4	72.1	1.0	1.0	"
" " (American), mean . . .	25	12.5	11.3	1.2	74.1	0.3	0.6	Johnson
" " " highest p.c. . .	—	13.6	14.1	2.0	78.1	1.2	—	"
" " " lowest p.c. . .	—	10.3	8.6	0.6	68.3	0.0	—	"
" germ . . .	4	8.5	27.6	11.5	45.6	2.0	4.8	Richardson
" bran (European) . . .	—	13.0	14.0	4.3	52.7	10.0	6.0	Various
" " (American) . . .	68	12.4	15.4	3.8	53.5	9.3	5.6	Johnson
" chaff . . .	—	14.3	4.5	1.4	34.6	36.0	9.2	Wolff
Dinkel bran . . .	—	13.0	14.0	4.3	54.9	8.2	5.6	"
" chaff . . .	—	14.3	3.5	1.3	32.6	40.0	8.3	König
Rye flour, fine . . .	—	14.0	10.2	1.6	72.6	0.6	1.0	König
" " coarse . . .	—	11.8	11.1	2.1	67.7	2.6	1.7	"
" bran . . .	—	12.4	14.7	5.2	58.7	6.2	4.8	Wolff
" chaff . . .	—	14.3	3.6	1.2	29.9	43.5	7.5	"
Oatmeal . . .	9	9.4	15.0	6.6	63.8	3.0	2.2	König (chiefly)
" (American) . . .	6	7.8	14.7	7.1	67.5	0.9	2.0	Johnson
" husk . . .	—	9.4	2.7	1.3	52.2	27.9	6.5	Wolff
" " (American) . . .	100	5.2	2.5	68.8	17.9	5.6	—	Richardson
Barley pearl . . .	4	14.9	7.6	1.0	75.1	0.6	0.8	Various
" husk . . .	—	14.3	3.0	1.5	38.2	30.0	13.0	Wolff
" malt . . .	—	7.5	9.4	2.3	69.8	8.7	2.3	"
" malt germs (combs) . . .	—	11.8	23.3	2.1	42.8	12.4	7.6	"
" brewer's grains . . .	—	76.1	4.9	1.5	12.9	3.5	1.1	"
Maize meal (American) . . .	60	15.6	9.2	3.8	68.0	2.0	1.5	Johnson
Rice feeding meal . . .	—	10.0	11.9	12.1	47.0	9.0	10.0	Various
" husk . . .	—	9.7	3.4	1.4	27.0	42.8	15.7	Wolff
Millet, <i>P. miliaceum</i> , husk . . .	—	11.2	4.8	2.3	29.0	40.8	11.2	"
" <i>S. tartaricum</i> , husk . . .	—	5.7	3.9	0.9	55.7	25.8	8.0	"

*Products of Grinding Barley.*

—	Water	Nitrogenous substance	Fat	Carbo-hydrates	Fibre	Ash
Coarse dust . . . . .	14.2	7.0	1.7	46.8	24.6	5.7
Fine " . . . . .	13.1	17.6	6.0	50.5	8.5	4.3
Pearl " . . . . .	13.3	12.1	3.4	67.2	1.8	2.2
" barley . . . . .	14.7	7.3	1.2	75.1	0.6	1.1

*Some Products of Rolling Wheat.*

—	Water	Nitrogenous substance	Fat	Carbo-hydrates	Fibre	Ash
Whole wheat . . . . .	9.6	12.8	2.3	71.8	1.6	1.9
Bran middlings . . . . .	8.2	16.5	5.5	56.8	6.1	6.9
Feed " . . . . .	8.5	16.5	5.0	62.1	4.1	3.8
Flour, low grade . . . . .	12.6	14.2	2.3	69.0	0.8	1.1
" baker's . . . . .	13.3	11.0	1.3	72.4	1.5	0.5
" patent . . . . .	13.0	10.0	0.9	75.6	0.2	0.3

The relative composition of the different parts of any grain can only be shown by a series of analyses made on the products from the same sample. Detailed analyses of the products obtained in grinding wheat between mill-stones have been made by Lawes and Gilbert (C. J. 10,

31), and by Dempwolf (A. 140, 343). The numerous products obtained in America by crushing between rollers have been analysed by Richardson (Am. G. 388, and Bulletin, 9, 78). As illustrations of the relative composition of successive layers of grain, both with and without adherent

chaff, we have given the analyses by Church of the products obtained in the preparation of pearl barley; and also a selection of the analyses made by Richardson of the numerous products obtained by crushing wheat.

The 'coarse barley dust' represents the external layers of the grain, including chaff; the 'pearl barley' consists wholly of endosperm. The external layer is seen to be richest in fibre and in ash; the second layer richest in nitrogenous matter and in fat; whilst the endosperm is richest in carbohydrates, and poorest in all other constituents. The wheat products exhibit the same general order of composition, from the external bran to the finest flour, with the difference that there is in this case no fibrous chaff poor in nitrogen to form the chief constituent of the outermost layer. The rice meal mentioned among the products of cereal grains consists of the outer layer of the grain, with some husk separated during cleaning; it is seen to be rich in fat, and far more nitrogenous than the cleaned rice.

The general composition of the embryo of wheat, as separated by the roller system, has been given in the table on p. 494. Individual analyses showed as much as 33.25 p.c. of nitrogenous substance, and 15.61 p.c. of fat. A detailed examination of the embryo has been made by Richardson and Crampton (B. 1886, 1180). It contains 15.18 p.c. of sugar, of which 80.90 p.c. is cane sugar. There is besides a highly dextrorotatory amorphous sugar, not reducing copper, but changed by yeast into a reducing sugar. The wheat embryo also contains *allantoin* (less than  $\frac{1}{2}$  p.c.); a drying oil; and a waxy, non-saponifying fat. Lenz (J. A. 1870-2, 2, 4) found in the embryo of wheat 28.4, in that of rye 20.7, in oats 26.5, in barley 28.4, and in maize 17.6 p.c. of nitrogenous substance. In the dry embryo of barley, Haberlandt found 22.42 p.c. of fat. Haberlandt (J. A. 1866, 107) separated the embryo and endosperm of maize, and found them to contain when dried at 60°:

—	Nitrogenous substance	Fat
Embryo . . . .	22.77	30.90
Endosperm . . . .	13.34	1.32

The greater part of the fat of the seed was thus contained in the embryo. Wagner and Meyer (J. A. 1883, 374) found in the embryo of rice 15.67 p.c. of nitrogenous substance, and 24.42 p.c. of fat.

We have just seen that some of the outer

layers of cereal grains are especially rich in nitrogenous matter; a larger proportion of this is, however, non-albuminoid, than is the case with the nitrogenous matter of the endosperm. Thus Church found that in pearl barley 92.4 p.c. of the nitrogen was albuminoid, while in 'fine dust' only 65.3 p.c. was in that condition.

Wigner (Analyst, 1878, 289, 303, 358) found the albuminoid nitrogen of wheat flour, mean of fifteen analyses, to be 90.2 p.c. of the total; while in the bran from the same grain the proportion was 68.1 p.c. Other chemists have found a larger proportion of albuminoid nitrogen in wheat bran, five analyses giving a mean of 82.5 p.c. of the total nitrogen. In rye bran one analysis showed 67.5 p.c. In rice meal two analyses gave 93.6 p.c. The smaller proportion of the nitrogen existing as albuminoids must, of course, be taken into account in estimating the nourishing value of the coarser meals and flours.

In malt six analyses show a mean of 79.2 p.c. of total nitrogen as albuminoids. In malt sprouts (malt dust or combs) eight analyses give a mean of 72.7 p.c. In brewers' grains two analyses show 97.6 p.c., the amide bodies having been dissolved out during mashing.

Wheat bran, according to Mège-Mouries (C. R. 37, 351; 38, 505; 42, 1122; 48, 431; 50, 467), contains a nitrogenous ferment capable of converting starch paste into dextrin, sugar, and lactic acid. This ferment he names *cercalin*.

The carbohydrates of the various parts of cereal grains are, of course, identical with those in the whole grain. Müntz found wheat bran especially rich in pectic bodies, the amount reaching 2 p.c. The proportion of true cellulose he found to be 20.5 p.c. The 'fibre' in the same sample was by the usual mode of estimation only 5.16 p.c.

3. *Straw*. The proximate composition of cereal straw given below is taken from Wolff's table of average compositions; that of maize cob is the average of seventeen American analyses.

The composition of straw is considerably affected by the character of the season, and to a smaller extent by that of the soil and manure. Illustrations of the influence of season and manuring upon the proportion of nitrogen and ash constituents in wheat straw will be found on p. 498. When the grain is prematurely or imperfectly ripened, the straw is much richer in nitrogen than when the development of the seed has been complete; in the latter case, a large part of the nitrogen and important ash constituent of the stem and leaf will have passed into the seed, in the former case they remain in the straw. For the same reason straw cut while yet

Average Composition of Cereal Straws.

—	Water	Nitrogenous substance	Fat	Carbohydrates	Fibre	Ash
Wheat straw . . . .	14.3	3.0	1.2	36.9	40.0	4.6
Spelt straw . . . .	14.3	2.5	1.4	31.8	45.0	5.0
Rye straw . . . .	14.3	3.0	1.3	33.3	44.0	4.1
Oat straw . . . .	14.3	4.0	2.0	36.2	39.5	4.0
Barley straw (winter) . . . .	14.3	3.3	1.4	32.5	43.0	5.5
" " (summer) . . . .	14.3	3.5	1.4	36.7	40.0	4.1
Maize straw . . . .	15.0	3.0	1.0	36.7	40.0	4.2
" cob . . . .	10.8	2.4	0.5	54.7	30.4	1.3



green is more nutritious than straw fully ripened. The part of the straw poorest in nitrogen is the stem; the leaf and empty ear are richer.

Few determinations of albuminoids have been made in straw; the variations are considerable. One analysis of rye straw showed no non-albuminoid nitrogen. Three analyses of oat straw showed 66.1, 78.2 and 94.4 of albuminoid nitrogen per 100 of total. Two analyses of barley straw showed 90.3 and 92.0 p.c. Two analyses of rice straw 87.6 and 88.5 p.c. Two analyses of millet straw 70.9 and 93.5 p.c. of the total nitrogen.

The fat of oat and rice straw has been examined by König (L. V. 13, 241). The saponifiable portion of the fat from oat straw consisted of *cerotic*, *palmitic*, and *oleic* acids; the unsaponified portion contains *ceryl* and other alcohols, with *cholesterin*.

According to Müntz, wheat straw contains a

little *glucose*, 0.27 p.c. in one instance; 1.2 p.c. of *pectic* bodies; and 0.5 p.c. of *gum*. It contains no starch. The chief constituent is *cellulose*, with its incrusting *lignose*. The amount of total fibre in straw is greatly underrated in ordinary analyses; the soluble carbohydrates shown by analysis consist, in fact, in greatest part of cellulose which has been converted into sugar during boiling with acid. Müller (Die Pflanzenfaser, 97) found 49.17 and 49.22 p.c. of true cellulose in wheat and rye straw. Müntz found 49.44 p.c. in wheat straw by dissolving the cellulose in Schweitzer's fluid and reprecipitating.

**II. Composition of the ash** 1. *Ash of whole grain*. The average composition of the ash of cereal grains is shown in the following table. The figures are taken from Wolf's Aschen-Analysen, 1880, excepting the analyses of *P. italicum* and *S. saccharatum* by Kellner.

Composition of the Ash of Cereal Grains.

—	Number of Analyses	Pure Ash in dry Grain	100 parts of pure ash contain								
			K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	Cl
Wheat (winter) . . . .	110	1.96	31.2	2.1	3.3	12.1	1.3	17.2	0.4	2.0	0.3
Spelt, with chaff . . . .	2	4.29	15.6	1.0	2.6	6.5	1.6	20.7	2.9	46.7	0.6
„ without chaff . . . .	4	1.68	30.1	4.8	4.3	12.4	1.5	15.2	—	1.0	—
Rye (winter) . . . . .	36	2.09	32.1	1.5	2.9	11.2	1.2	17.7	1.3	1.4	0.5
Oats, with husk . . . .	57	3.12	17.9	1.7	3.6	7.1	1.2	25.6	1.3	39.2	0.9
„ naked . . . . .	4	2.07	28.0	—	7.5	10.1	1.5	17.7	—	1.2	0.3
Barley, with husk . . . .	57	2.61	20.9	2.4	2.6	8.8	1.2	35.1	1.8	25.9	1.0
„ naked . . . . .	3	2.13	28.5	1.8	3.1	12.0	1.9	17.1	2.9	3.6	—
Maize . . . . .	15	1.45	29.8	1.1	2.2	15.5	0.8	15.6	0.8	2.1	0.9
Rice, with husk . . . .	2	8.21	17.5	5.5	4.0	10.8	1.8	40.6	0.9	18.3	0.9
„ without husk . . . .	5	0.39	21.7	5.5	3.2	11.2	1.2	53.7	0.6	2.7	0.1
Millet, <i>P. miliaceum</i> , with husk . . . . .	3	3.43	11.4	1.3	0.6	9.6	1.1	21.9	0.2	53.0	0.5
Millet, <i>P. miliaceum</i> , without husk . . . .	1	1.46	17.4	5.3	—	17.0	1.5	49.2	1.3	8.3	—
Millet, <i>P. italicum</i> , without husk . . . .	1	1.26	20.6	3.3	2.4	11.1	0.4	39.6	3.3	11.6	3.7
Millet, <i>S. saccharatum</i> , with husk . . . . .	1	2.72	14.9	8.4	0.7	13.2	0.4	24.8	0.8	36.8	0.1
Millet, <i>S. saccharatum</i> , without husk . . . .	1	5.26?	21.4	4.9	2.6	14.5	1.8	49.7	2.5	0.2	1.4
Millet, <i>S. tartaricum</i> , with husk . . . . .	1	1.86	20.3	3.3	1.3	14.8	1.9	50.9	—	7.5	—

The characteristics of the grain ash are a very high percentage of *phosphoric acid* and *potash*; *magnesia* stands next in order among the constituents, it is especially abundant in maize and some of the millets. *Soda* appears in very small quantity in good analyses made on clean seed; the sodium salts are frequently external, and may be removed to a considerable extent by washing the grain. *Silica* is present in very small amount when the grain is free from husk, as in wheat or rye, while grains with a husk contain a large quantity. The ash of oats and barley appears of very different composition from that of wheat, owing to the large proportion of silica present; when, however, these grains are deprived of husk, their ashes become quite similar to wheat in composition. *Chlorine* is absent in many analyses of grain ash, and the amount is always very small. The quantity in the ash is probably somewhat below that origi-

nally present in the grain. The *sulphuric acid* in the ash is apparent in excess of the sulphates originally present in the grain. Wolf (Aschen-Analysen, 1871, 12, 22, 30) found no ready formed sulphates in wheat, barley, or oat plants. Scheven found a small quantity of ready-formed sulphates in barley plants, and a larger quantity in the ash. Arendt found sulphates in the leaves of oat plants. The total quantity of *sulphur* in cereal grains has been determined by several chemists. The results obtained by Way are very high. The more recent determinations of Wolf (*v. supra*) show the following amounts of sulphur in 100 parts of dry substance. Wheat grain, 0.157; oat grain, 0.155, 0.160; barley grain, 0.160. 9.173. Knopp found in maize grain, 0.100 0.146. *Manganese* is frequently present in small quantity in the ash of cereal grains. In the ash of wheat grain grown at Rothamsted the average amount is about 0.26 p.c. of Mn<sub>2</sub>O<sub>3</sub>.

2. *Ash of parts and products of cereal grains.*  
 --The following ash analyses of the parts and products of cereal grains illustrate the distri-

bution of the ash constituents in the different parts of the seed.

*Ash Analyses of Parts and Products of Cereal Grains.*

—	Number of analyses	Pure ash in dry	In 100 parts of pure ash								
			K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	Cl
Wheat flour, fine . . .	9	0.51	3.4	0.8	6.9	8.1	0.5	49.8	—	—	—
„ „ coarser . . .	7	1.27	30.8	0.9	5.1	12.2	0.8	50.2	—	0.3	0.1
„ bran . . .	4	6.16	28.5	0.7	2.9	16.7	0.6	50.3	0.1	0.5	—
„ chaff . . .	1	10.73	9.1	1.8	1.9	1.3	0.4	4.3	—	81.2	—
Spelt chaff . . .	1	9.50	9.5	0.3	2.4	2.5	0.5	7.3	2.3	74.2	—
Rye flour . . .	1	1.97	38.4	1.8	1.0	8.0	2.5	48.3	—	—	—
„ chaff . . .	1	9.65	6.3	0.3	4.2	1.4	0.2	6.7	0.2	80.3	0.5
Oat bran . . .	3	4.04	14.2	0.8	4.0	3.0	1.2	4.6	3.8	66.9	1.5
„ chaff . . .	6	8.31	6.3	4.1	5.6	2.1	1.5	1.9	4.9	70.7	1.2
Barley, 'fine dust' . .	2	2.43	26.0	1.9	2.7	13.1	2.2	51.1	1.5	1.4	—
„ 'coarse dust' . .	1	5.63	16.8	1.4	3.7	6.3	1.7	18.5	1.9	48.7	1.3
„ awn . . .	1	13.95	7.9	1.0	10.6	1.3	1.5	2.0	3.1	72.2	0.7
„ malt combs . . .	3	7.35	30.81	1.8	2.9	2.8	1.6	27.0	4.0	22.1	6.9
„ brewer's grains . .	2	4.54	3.27	0.6	14.0	10.0	1.1	37.2	—	33.2	—
Maize cob, empty . .	1	0.52	50.9	1.3	3.7	4.4	0.2	4.7	2.1	28.4	5.4
Rice feeding meal . .	2	6.08	11.1	2.1	2.2	17.4	5.5	43.1	0.4	18.9	—
„ husk . . .	1	17.10	1.5	0.3	0.5	0.1	0.5	2.7	0.4	93.2	0.2

In fine wheat flour, representing the interior and more starchy portion of the grain, the proportion of ash is very small, and this ash is richer in potash and lime, and poorer in magnesia, than that of the whole grain. In wheat bran the proportion of ash is about 12 times greater than in fine flour, and the ash is poorer in potash and lime and richer in magnesia than that of the whole grain. The percentage of phosphoric acid in the ash tends to increase towards the exterior of the grain. This increase is rather considerable in the analyses of wheat products by Lawes and Gilbert (C. J. 10, 31), but is only slight in the results obtained by Dempwolf (A.

110, 313). The same general relation between the ash of the interior and exterior layers of the grain is indicated in the ash analyses of barley 'fine dust,' which consists chiefly of the external layer of the kernel, and in the analysis of rice 'feeding meal,' which represents the skin of the rice with a portion of the husk. The ash of the chaff and husk of the grain is entirely distinct in composition from that of the seed itself; it is extremely rich in silica, containing more of this constituent than the straw itself.

3. *Ash of straw.*—The average composition of the straw ash of cereals is given by Wolff as follows:—

*Ash Analyses of Straw.*

—	Number of analyses	Pure ash in dry	100 parts of pure ash contain								
			K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	Cl
Wheat straw (winter) .	18	5.37	13.7	1.4	5.8	2.5	0.6	4.8	2.5	67.5	1.7
„ „ (summer) . . .	7	4.45	28.9	2.7	6.9	2.5	0.7	5.2	3.1	47.6	2.2
Spelt „ (winter) . .	2	5.85	10.4	0.5	5.7	1.9	0.8	5.1	2.3	71.8	1.1
Rye „ . . .	25	4.46	22.6	1.7	8.2	3.1	1.9	6.5	4.3	49.3	2.2
Oat „ . . .	38	7.17	26.4	3.3	7.0	3.7	1.2	4.6	3.2	46.7	4.4
Barley „ . . .	30	5.35	23.3	3.5	7.2	2.6	1.1	4.2	3.9	51.0	3.2
Maize „ . . .	1	5.33	36.3	1.2	10.8	5.7	2.3	8.3	5.3	28.8	1.4
<i>S. saccharatum</i> straw	1	3.70	15.3	7.3	17.1	1.5	1.5	9.2	3.9	43.3	0.9

The quantity of ash ereditd to oat straw is probably excessive, as many of the specimens had grown in rich soil. Next to *silica* the chief ingredient of straw ash is *potash*; the amount is very variable. In straw ash the *lime* considerably exceeds the *magnesia*; the relation observed in the grain ash is thus reversed. *Soda* and *chlorine* are always present in straw ash. The remarks already made as to the *sulphates* in grain ash apply equally in the case of straw. The total *sulphur* found by Wolff in wheat straw amounted to 0.084 and 0.111 p.c.; in oat straw to 0.092 and 0.109 p.c.; in barley straw to 0.100,

0.101, and 0.151 p.c. of the dry substance. *Silica* is by far the most abundant constituent of straw ash; it is very variable in amount. Winter wheat and spelt appear to contain a larger proportion than the spring sown cereals. The silica in the living plant is insoluble in cold water, save a portion in the lower part of the stem (Arendt).

The presence of a large quantity of silica in graminaceous plants is one of their distinguishing characteristics, and clearly indicates a power on their part of assimilating the silicates of the soil. Silica was long supposed to be essential to

the nutrition of graminæ, and to be the material which chiefly determined the stiffness of the straw. The experiments of Sachs, Knop, and many other recent investigators, on the growth of oats and maize in solutions containing no silica, have shown that silica is not essential to plant growth or to the development of the seed, nor does its absence materially affect the stiffness of the straw. The silica of the graminæ is in fact to be regarded to a great extent as an excretion thrown off on the surface of the plant, and especially accumulating in the upper portion. Some very careful recent experiments of Kreushage and Wolff (L. V. 30, 161) indicate, however, that silicates are not altogether useless to the plant. Oat plants grown in solutions containing silicates did not yield any distinctly greater weight of total produce than others grown without silicates; but the former yielded a larger proportion

of corn. There was, in fact, a more thorough transference of organic and mineral constituents from the roots, stem, and leaves, to the seed, during the ripening period, when the plant was supplied with silica, than when it was without it. As phosphates also favour seed formation, it appears possible that the presence of silica economises phosphates; but this is not yet established in a practical manner.

The harvested straw of cereals really consists of several distinct portions of the plant, as the stem, leaf, and ear. Each of these has a characteristic composition. The following table gives the analyses by Bretschneider of the ash of the stem, leaf and leaf-sheath, and ear with seed, of an oat plant in three stages of growth.

The leaf is seen to contain twice as much ash as the stem. The stem ash contains a much larger proportion of potash, also more

*Percentage Composition of Ash of various parts of Oat Plant.*

	Stem				Leaf with sheath				Ear with seed	
	June 29	July 8	July 28	Aug. 6	June 29	July 8	July 28	Aug. 6	July 28	Aug. 6
Ash in dry . . .	5.34	4.76	5.03	5.05	11.11	10.14	12.21	11.37	4.29	4.42
K <sub>2</sub> O . . . . .	31.5	29.7	37.0	33.7	20.8	17.6	10.1	7.7	15.9	11.5
Na <sub>2</sub> O . . . . .	11.9	9.4	7.7	8.9	9.3	7.8	3.1	2.8	0.5	2.0
CaO . . . . .	4.0	4.6	4.0	5.2	8.3	9.5	8.7	9.7	4.3	4.1
MgO . . . . .	4.1	5.1	4.7	4.2	4.7	5.5	4.8	4.6	5.4	6.8
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.4	0.5	0.2	0.3	0.4	0.5	0.3	0.4	0.2	0.4
P <sub>2</sub> O <sub>5</sub> . . . . .	11.1	11.2	6.3	3.4	5.1	5.4	3.2	2.3	16.9	20.5
SO <sub>3</sub> . . . . .	3.5	2.1	4.3	5.2	4.2	3.5	2.0	2.7	1.5	2.4
SiO <sub>2</sub> . . . . .	30.8	34.7	31.2	35.4	46.4	49.3	67.2	69.5	54.6	51.9
Cl . . . . .	3.5	3.6	6.0	4.2	1.2	1.3	0.8	0.5	0.6	0.4

*Nitrogen and Ash Constituents of Wheat Grain grown at Rothamsted.*

—	Nitrogen in dry	Pure ash in dry	In 100 parts of pure ash								
			K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	Cl
Unmanured, mean 16 years . . . . .	1.90	2.01	32.96	0.62	2.83	10.33	1.03	49.71	1.31	1.16	0.06
Unmanured, highest percentages . . . . .	2.17	2.36	35.49	1.18	3.39	11.67	1.37	52.56	2.40	2.51	0.24
Unmanured, lowest percentages . . . . .	1.65	1.88	29.66	0.41	2.51	9.14	0.51	45.55	0.65	0.45	0.00
Farmyard manure, mean 16 years . . . . .	1.83	2.01	31.57	0.59	2.59	11.11	0.84	51.70	0.79	0.79	0.03
Farmyard manure, highest percentages . . . . .	2.19	2.20	35.46	0.84	2.88	12.77	1.23	54.69	2.35	1.56	0.11
Farmyard manure, lowest percentages . . . . .	1.52	1.85	27.22	0.28	2.34	10.13	0.43	47.05	0.03	0.49	0.00

*Nitrogen and Ash Constituents of Wheat Straw.*

Unmanured, mean 16 years . . . . .	0.50	6.44	14.56	0.59	3.89	2.12	0.84	3.79	3.14	69.41	1.89
Unmanured, highest percentages . . . . .	0.85	8.33	20.68	2.12	6.10	3.50	1.64	5.96	4.76	76.37	3.19
Unmanured, lowest percentages . . . . .	0.33	4.82	10.54	0.26	2.52	1.03	0.32	2.98	2.05	62.72	1.08
Farmyard manure, mean 16 years . . . . .	0.44	6.52	18.33	0.51	4.13	1.52	0.52	3.79	3.00	65.75	3.16
Farmyard manure, highest percentages . . . . .	0.73	7.91	25.62	0.94	5.46	2.14	0.85	6.21	4.62	73.07	5.02
Farmyard manure, lowest percentages . . . . .	0.25	4.90	12.86	0.00	3.20	1.06	0.18	2.98	2.04	57.87	1.84



soda, and more phosphoric acid and chlorine than the leaf ash. The leaf ash is richer in lime and much richer in silica. Arendt has separately analysed the different parts of the oat stem, and the upper and lower leaves. The total ash is much more abundant in the upper than in the lower portion of the stem, and in the earlier stages of growth nearly all the constituents of the ash show a similar distribution. As maturity advances, silica accumulates to a considerable extent in the upper stem. Silica is also more abundant in the upper than in the lower leaves. The extremity of the leaf is, according to Norton, richer in ash than the base. The ear, as the seed develops, becomes the part richest in phosphoric acid. For details we must refer to the original papers, the principal of which will be presently noticed.

4. *Effect of season and manuring on the ash.* We shall best illustrate the variations which these conditions produce in the ash constituents of cereals by giving examples of the composition of wheat grain and straw grown at Rothamsted (C. J. 45, 305).

Wheat has been grown continuously in Broadbalk field since 1844, one plot entirely unmanured, another with 14 tons of farmyard manure each year, the remaining plots with other manures. The table on p. 498 gives the mean composition of the ash of the wheat grain and straw grown without manure, and with farmyard manure, during a period of sixteen years (1848-63); also the highest and lowest percentages of each ash constituent during that period. The figures thus illustrate the extent of variation produced by season during sixteen years, both without manure, and with an abundant manuring.

The variations in the ash constituents of the grain are seen to be but small; they depend chiefly on the degree of development which the seed attains. The variations exhibited by the straw are far more considerable, many of the constituents being almost twice as abundant in some years than in others. The causes of variation are frequently complicated. They depend—

(1) On the conditions regulating the supply of ash constituents. A dry season during growth is sure to determine a paucity of ash constituents in the crop, while a wet growing season enables the crop to take up a large supply.

(2) The general conditions as to light and heat determine the amount of carbonaceous matter produced, and thus directly influence the proportion of ash constituents in the final crop. The produce of a warm season, under equal conditions as to rain supply, will always contain a smaller proportion of ash constituents than the produce of a cold season.

(3) The conditions as to light and heat at certain stages of growth have a decisive influence on the relative composition of the straw and corn. If the season is favourable to the formation of seed, the leaves, stem, and roots are gradually exhausted of phosphoric acid and potash, which are transferred to the seed. In a season unfavourable to the production of seed the phosphoric acid and potash remain to a great extent in the straw.

(4) The degree of development reached by the grain affects its composition. Very immature grain is rich in potash and poor in phosphoric

acid. On the other hand a grain ripening under unfavourable conditions and yielding a low proportion of flour and much bran, will be relatively rich in nitrogen, phosphoric acid, and magnesia, as may be seen by comparing the ash analyses of flour and bran already given. In seasons of the best development there is no excess of potash or phosphoric acid in the grain. Hard wheat is generally richer in phosphoric acid than soft wheat, and spring-sown richer than autumn-sown.

(5) The amount of rain at harvest time will considerably influence the proportion of soluble ash constituents found in the straw and chaff, dead tissues being far more subject to the action of water than living ones. A maximum content of alkali salts in the straw is determined by a wet summer and a dry harvest.

The influence of differences of manuring on the composition of the ash of wheat grain and straw is shown by the adjoining table. The figures are in every case the mean of four analyses, representing the composition of the corn and straw in 1852, 1856, 1858, and 1863. The same manures were applied every year without intermission to the same plot of land, and wheat continuously grown. The mixed cinereal manure consisted of superphosphate, and the sulphates of potassium, sodium, and magnesium.

The influence on the composition of the grain of widely different supplies of ash constituents to the soil is seen to have been very small. The quantity of grain produced was indeed very different with the different manures, reaching a maximum where a full supply both of ash constituents and ammonia was furnished to the crop, but the proportion of ash constituents in the grain varied but little. With no ash constituents supplied (ammonium salts only), the phosphoric acid is at a minimum. With a nearly complete manure without potash (ammonia and superphosphate) potash is at a minimum.

The composition of the straw is far more affected by difference of manuring than that of the corn; the greatest difference observed is in the proportion of potash. A plant may take up alkalis from the soil far in excess of its requirements; these, however, are not stored in the seed, but will be found in the straw.

III. *Life history.* The composition of the different parts of cereal plants, and of the whole plant in different stages of growth, have been studied by the following investigators:—*Wheat*, by Anderson (Trans. Highland Soc. 10, 383), Pierre (J. A. 1864, 127; 1866, 163; 1868-9, 263; A. a. 2, 59), Wolff (Aschen-Analysen, 1871, 12), Ritthausen u. Arendt (*ibid.* 13). *Rye*, by Schulz-Fleeth, Ritthausen, Heiden Gruber u. Fritsche (*ibid.* 16), Dehérain et Meyer (A. a. 8, 23). *Oats*, by Norton (Am. S. [2] 3, 222, 318), Breitschneider (J. pr. 76, 193), Arendt (J. A. 1858-9, 124), Fittbogen (J. A. 1864, 128), Wolff (Aschen-Analysen, 1871, 29), Ritthausen (*ibid.* 30), Dehérain, Meyer et Nautier (A. a. 7, 197, 208; 8, 380). *Barley*, by Schieven (J. pr. 68, 193), Wolff (Aschen-Analysen, 1871, 21), Fittbogen (*ibid.* 1880, 12). *Maize*, by Leclerc (*ibid.* 1880, 18), Barral (*ibid.* 19), Grandeau (*ibid.* 19), Hornberger u. Raumer (J. A. 1882, 159), Portele (L. V. 32, 241). *Millet* (*S. italica*), by

*Nitrogen and Ash Constituents in Wheat Grain grown at Rothamsted with various manures.*

Manuring	Nitrogen in dry	Pure ash in dry	In 100 of pure ash								
			K <sub>2</sub> O	Na <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub>	SiO <sub>2</sub>	Cl
Ammonium salts . . .	2.03	1.75	32.0	0.44	3.76	11.5	0.61	48.9	1.69	1.01	0.19
Ammonium salts and superphosphate . . .	1.92	1.85	30.3	0.49	3.83	11.2	0.95	51.3	1.02	0.90	0.03
Ammonium salts, super- phosphate and potash .	1.85	1.86	31.7	0.35	2.92	11.1	0.87	51.5	0.73	0.72	0.02
Ammonium salts and mixed cinereals . . .	1.87	1.88	31.5	0.51	2.79	11.8	0.61	51.5	0.50	0.84	0.01
Mixed cinereals . . .	1.74	2.02	31.4	0.50	2.82	11.0	0.61	52.1	0.67	0.90	0.01

*Nitrogen and Ash Constituents in Wheat Straw variously manured.*

Ammonium salts . . .	0.58	5.09	14.0	1.18	6.68	1.75	0.56	2.68	4.55	66.8	2.38	
Ammonium salts and superphosphate . . .	0.46	5.40	9.2	1.41	6.61	1.82	0.82	3.09	3.35	72.3	1.90	
Ammonium salts, super- phosphate and potash .	0.34	5.45	20.6	0.44	4.83	1.44	0.73	2.73	3.31	62.3	4.59	
Ammonium salts and mixed cinereals . . .	0.51	5.47	19.6	0.76	5.15	1.42	0.71	3.25	3.62	62.1	4.44	
Mixed cinereals . . .	0.44	6.83	14.3	1.23	3.76	1.33	0.75	3.98	4.01	69.2	1.87	

*Ash Constituents of Grain per 1000 of dry substance.*

Ammonium salts . . .	—	—	5.65	0.08	0.66	1.99	0.11	8.46	0.31	0.17	0.03	
Ammonium salts and superphosphate . . .	—	—	5.68	0.09	0.71	2.05	0.17	9.44	0.20	0.16	0.01	
Ammonium salts, super- phosphate and potash .	—	—	6.01	0.66	0.54	2.03	0.15	9.52	0.15	0.13	0.01	
Ammonium salts and mixed cinereals . . .	—	—	5.99	0.10	0.52	2.18	0.11	9.62	0.10	0.16	—	
Mixed cinereals . . .	—	—	6.35	0.10	0.56	2.22	0.12	10.51	0.13	0.18	—	

*Ash Constituents of Straw per 1000 of dry substance.*

Ammonium salts . . .	—	—	6.99	0.57	3.31	0.87	0.27	1.30	2.15	34.48	1.24	
Ammonium salts and superphosphate . . .	—	—	4.85	0.77	3.59	1.00	0.44	1.65	1.78	39.08	1.05	
Ammonium salts, super- phosphate and potash .	—	—	11.50	0.25	2.64	0.79	0.36	1.43	1.81	33.69	2.60	
Ammonium salts and mixed cinereals . . .	—	—	10.90	0.40	2.82	0.77	0.39	1.76	1.99	33.70	2.51	
Mixed cinereals . . .	—	—	9.60	0.83	2.57	0.91	0.53	2.74	2.72	47.46	1.24	

Metzdorf (J. A. 1860 61, 136), *S. saccharatum*, plant food removed from the soil in pounds per acre by average crops of wheat, barley, oats, and by Meunier (A. a. 7, 73).

IV. Food requirements. The quantity of

maize, is about as follows:

*The Weight and Average Composition of Cereal Crops in pounds per acre.*

—	Weight of crop		Total pure ash	Nitro- gen	Sulphur	Potash	Soda	Lime	Maga- nesia	Phos- phoric acid	Chlor- ine	Silica
	At harvest	Dry										
Wheat grain 30 bushels.	lbs. 1,800	lbs. 1,530	lbs. 30	lbs. 33	lbs. 2.7	lbs. 9.3	lbs. 0.6	lbs. 1.0	lbs. 3.6	lbs. 14.2	lbs. 0.1	lbs. 0.6
" straw . . .	3,158	2,653	142	15	5.1	19.5	2.0	8.2	3.5	6.9	2.4	96.3
Total crop .	4,958	4,183	172	48	7.8	28.8	2.6	9.2	7.1	21.1	2.5	96.9
Barley grain 40 bushels.	2,080	1,747	46	35	2.9	9.8	1.1	1.2	4.0	16.0	0.5	11.8
" straw . . .	2,447	2,080	111	13	3.2	25.9	3.9	8.0	2.9	4.7	3.6	56.8
Total crop .	4,527	3,827	157	48	6.1	35.7	5.0	9.2	6.9	20.7	4.1	68.6
Oats grain 45 bushels .	1,890	1,625	51	38	3.2	9.1	0.8	1.8	3.6	13.0	0.5	19.9
" straw . . .	2,835	2,353	140	17	4.8	37.0	4.6	9.8	5.1	6.4	6.1	65.4
Total crop .	4,725	3,978	191	55	8.0	46.1	5.4	11.6	8.7	19.4	6.6	85.3
Maize grain 30 bushels.	1,630	1,500	22	28	1.8	6.5	0.2	0.5	3.1	10.0	0.2	0.5
" stalks &c. . .	2,208	1,877	99	15	—	29.8	—	—	—	8.0	—	—
Total crop .	3,838	3,377	121	43	—	36.3	—	—	—	18.0	—	—

**CERESIN.** Ceresin occurs in commerce in the form of thin round masses several inches in diameter, harder than wax, of a dazzling white colour; inodorous, and transparent at the edges. The fracture is somewhat similar to that of wax, but ceresin does not become plastic in warm water. The melting point is between  $75^{\circ}$  and  $80^{\circ}$ . It is not attacked by acids, either in the cold or when heated; nor by alkalis, which do not saponify a trace of it. It is entirely volatilised at a high temperature without alteration. Ceresin is apparently a paraffin; it does not appear to be obtained from coal-tar, but from Galician 'earth-wax' i.e. ozokerite. It is used as a substitute for beeswax (S. C. I. 11, 372).

**CERIN**  $C_{20}H_{42}O$ ? A crystalline substance present in cork to the extent of about 2 p.c. and extracted by chloroform. Insoluble in water. By treatment with nitric acid yields *ceric acid*. Kögler, Ar. Ph. [3] 22, 217; Döpping, A. 45, 289.

**CERINE** v. WAX.

**CERISE.** A trade name for a variety of aniline red and acid magenta.

**CERIUM METALS AND EARTHS.** A considerable number of metals are included under this heading. Each invariably occurs with a number of metals of the same group, and, on account of the great resemblance between their reactions many of them can only be separated by the most laborious fractional precipitation or crystallisation, or are only distinguished by means of the spectroscope.

A mineral *gadolinite* from Ytterby was shown in 1794 by its discoverer Gadolin to contain a new oxide to which Ekeberg gave the name *yttria*. Klaproth in 1803 isolated from a Swedish mineral *ochroite* a new oxide which he called *ceria*. This so-called yttria was shown by Berzelius in 1819 to contain ceria, and Mosander subsequently found *lanthanum*, *didymium*, *terbium*, and *erbium* in that earth.

A number of other oxides have since been isolated from the earths associated with cerium. Marignac has separated the colourless oxide *ytterbia* from gadolinite, and has shown its presence in the rose-coloured oxide then known as *erbia*. Two other oxides were separated during the fractionation of erbia by Clève, and called by him *holmia* and *thulia*. Holmia appears to be identical with Soret's X and with Delafontaine's *phillipia*. It has been shown by Boisbaudran to consist of two substances, for one of which he retains the name holmia, while he names the second *dysprosium*. An oxide *mosandria* separated by J. L. Smith from North Californian *samaraskite*, appears to be a mixture of terbium and Marignac's  $Y_a$  (Boisbaudran, Marignac). Crookes has also observed the presence of yttria in mosandria. A new earth obtained by Delafontaine in 1878 has since been divided by him into two constituents, one of which he names *decipia*, while the other appears to be identical with Marignac's  $Y_{\beta}$ , and with an oxide separated from samarskite in 1879 by Boisbaudran and named *samarita*.

A new metal discovered by Nilson in 1879 during the separation of ytterbium and erbium is named *scandium*. Its atomic weight (44) and its properties correspond with those of the element *ekaboron* predicted by Mendeleff.

Thalen in 1868 and Clève in 1882 had observed a new line in a fraction separated from didymia. Brauner in 1882 suspected the presence of at least three bodies in didymia, and Auer von Welsbach in 1885, by many hundreds of fractional crystallisations of didymium nitrate, separated it into two distinct substances, one giving leek-green salts and a dark-brown oxide, to which he gave the name *praseo-didymium*, and a second, which he called *neo-didymium*, yielding splendid amethyst salts and an oxide which when ignited was blue.

Crookes, Boisbaudran, and Demarcay next showed that praseo- and neo-didymium themselves consist of several elements.

From spectroscopic evidence Crookes considers that yttrium consists of not less than five metals, while according to Krüss and Nilson most of the other cerium metals are complex bodies. There appear to be, in erbium two, in dysprosium three, in samarium two or perhaps three, in holmium four, in thulium two, and in didymium nine or ten distinct bodies. Whether these constituents are further divisible has still to be determined.

The principal minerals in which these metals occur are from Siberia, Scandinavia, and Greenland, and are principally silicates, but phosphates, tantalates, titanates, and fluorides also exist. Cerite occurs at Bastnäs, *orthite* in Greenland, *gadolinite* at Ytterby, *wöhlerite*, at Hitterö and Brevig, *fergusnite* at Arendal and Ytterby, *cuxenite* at Hitterö, *thorite* at Brevig, Hitterö, and Arendal. *Samaraskite* and *columbite* occur in comparatively large quantities in North California and other localities in the United States and in Quebec.

These metals are also found in small quantities, generally associated with calcium, in the ashes of plants, and in bone ash, various limestones, apatites, secheilites, &c. Yttrium and samarium appear to be almost universally distributed (Crookes). Strohecker (J. pr. [2] 33, 132) has stated that from 9-13 p.c. of cerium hydroxide, together with small quantities of the other earths, occur in the red clays of Hainstadt, and attributes the orange red to 'leather' colour of the bricks made from it to the presence of these earths. Blomstrand (J. pr. [2] 33, 483), and Schertel (B. 19, 1368), do not confirm the presence of these earths.

**CERIUM.** Symbol Ce. At. w. 139.9 (H. Robinson, Brauner). Metallic cerium may be prepared by electrolysis of the fused chloride. It resembles iron in colour and lustre, and melts below the melting-point of silver but above that of antimony. It is ductile and malleable, its sp.gr. after fusion under sodium chloride is 6.728. Cerium tarnishes in moist air and slowly decomposes water with formation of the hydroxide. It burns more readily and more brilliantly than magnesium, and combines directly with the halogens.

Cerium forms three oxides, cerium sesquioxide  $Ce_2O_3$ , cerium dioxide  $CeO_2$ , and cerium trioxide  $CeO_3$ .

Cerium sesquioxide is a bluish-green powder which is not reduced when heated in hydrogen. It dissolves in acids with formation of *cerous* salts.



**Cerous chloride**  $\text{Ce}_2\text{Cl}_6$ . The anhydrous chloride is an easily fusible deliquescent salt soluble in water with evolution of heat. At dull redness it is decomposed by oxygen with liberation of chlorine.

**Cerous sulphate**  $\text{Ce}_2(\text{SO}_4)_3$ . The acid sulphate of cerium has been used for the development of aniline black. According to W. Kruis (D. P. J. 212, 347) and Bührig (D. P. J. 231, 77), its effect is superior to that of vanadium. As the presence of the associated metals is not injurious, 1 kilo. of finely divided cerite may be at once treated with its own weight of sulphuric acid and digested at a gentle heat with occasional stirring. Much heat is developed and a portion of the sulphuric acid is volatilised, leaving a dry grey mass which is powdered, mixed with 250-300 grams sulphuric acid, digested at a gentle heat for some days, and expelled by heating the free acid on a sand bath. The grey powder is thrown in small portions into cold water with constant agitation and frequent addition of ice to keep down the temperature, the mixture is digested with occasional stirring for a day or two and the liquid is decanted; the residue is again treated with water to remove all soluble constituents.

One kilo. of cerite produces about 20 litres of solution, which may be used directly or may be evaporated, the clear rose-coloured crystals obtained being dissolved in cold water. Of the above solution 10 c.c., containing about  $\frac{1}{2}$  gram of cerium sesquioxide, is sufficient to develop over 110 litres of the printing solution, containing over 6 kilos. of the aniline salt.

The cloth being printed, is aged at 38-43° for about eight hours, the deep blue-black colour characteristic of the cerium salt being developed in a weak alkaline bath.

Cerous bromide, iodide, fluoride, sulphide, &c., and many double salts are also known. The insoluble cerous oxalate and the soluble double citrates, tartrates, and lactates of cerium and potassium, sodium, or ammonium, are used medicinally.

Cerium oxalate has proved a useful sedative in sickness and hysteria. It is said to be a good specific against sea-sickness.

Cerium dioxide is soluble in acids, forming, in the case of hydrochloric acid, cerous chloride with evolution of chlorine. It dissolves in nitric acid, and on addition of ammonium nitrate a double crystalline salt, *ammonium ceric nitrate*  $2\text{Ce}(\text{NO}_3)_6 \cdot \text{NH}_4\text{NO}_3 \cdot 3\text{H}_2\text{O}$  is produced.

**CEROSILINE** *v.* WAX.

**CEROXYLIN** *v.* WAX; also RESINS.

**CERUIEIN** *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

**CERUSITE**. Native lead carbonate *v.* LEAD.

**CERYL ALCOHOL** *v.* WAX.

**CETINE** *v.* WAX.

**CETYL ALCOHOL** *v.* SPERMACETI.

**CEVADINE** *v.* VEGETO-ALKALOIDS.

**CEYLON MOSS** *v.* ALGÆ.

**CHAGRAL GUM** *v.* GUMS.

**CHALCANTITE**. A native copper sulphate, found at Capo Calamita as a crust or efflorescence on iron ores.

**CHALCOITE**. Cuprous sulphide, *v.* COPPER.

**CHALCOTRICHITE**. Native copper suboxide, *v.* COPPER.

**CHALK** *v.* CALCIUM.

**CHALK, FRENCH**. Steatite or soap stone.

**CHAMOMILE OIL** *v.* OILS, ESSENTIAL.

**CHAMOTTE**. A mixture of fire-clay and burnt pottery used for making fire-bricks, crucibles, pipes, &c.

**CHARCOAL** *v.* CARBON and FUEL.

**CHAVICIC ACID** *v.* Pepper resin, art. RESIN.

**CHAYICIN** *v.* Pepper resin, art. RESIN.

**CHAY or C-HAYA ROOT**. The root of *Oldenlandia umbellata*, used in India as a substitute for madder.

**CHEESE**. The curd of milk compressed into a solid mass. Cheese may be prepared from the milk of any animal, but it is usually obtained from that of cows. The casein of fresh milk is precipitated by rennet and carries with it most of the fat as well as some portion of milk-sugar. Cheese may also be made from sour milk without the addition of rennet, the lactic acid contained in it being sufficient to precipitate the casein; but for the most part fresh milk is employed. The time of coagulation depends upon the strength and quantity of the rennet used and upon the temperature of the milk, an average of 80°F. being the most suitable, although this varies slightly according to the warmth of the weather. In the ordinary course coagulation is complete in from forty to sixty minutes. If the necessary time is not given, the curd will be soft and difficult of separation from the whey; if, on the other hand, the time is exceeded, the curd will be tough and leathery. When colouring matter such as annatto or saffron is employed, it is usually added at the time of introducing the rennet. When the milk is completely coagulated, the curd is broken down by means of a knife or an apparatus of wire meshes, after which the whey or residual liquor is drawn off. The curd is then allowed to stand about an hour, during which time a certain amount of acidity is induced. This acidulation may also be effected by other means, such as heating the mixture of curd and whey to a temperature of 98°F., or by adding a small quantity of sour milk to the fresh milk at the time of adding the rennet. The quantity of salt used is regulated by the richness or poverty of the fat, since less is required to prevent excessive fermentation in a rich than in poor curd. After being collected and bound into the required shape, the curd is pressed for two or three days and finally dried and ripened in a curing room, in which the temperature is kept as nearly as possible at 70°F. Any variation from this temperature is prejudicial.

There are, however, numerous slight variations of practice in the preparation of cheese which in their effect produce a marked distinctiveness and result in a very large number of kinds: such variations consist, *e.g.*, in the quality and condition of the milk employed, the temperature maintained during the operations involved, and the amount of fermentation permitted.

The essential constituents of cheese are casein and milk-fat, with variable proportions of water, lactic acid, and mineral matter, including a small proportion of salt added in the manufacture.

## Composition of Cheese (Bell).

Description	100 parts contain					Proportion of fat in 100 parts of dry cheese	Proportion of fat in 100 parts of casein and fat	Salt per cent. in cheese	Percentage composition of fat	
	Water	Fat	Casein or Nitrogenous matter	Free acid as lactic	Ash				Soluble acids	Insoluble acids
Stilton . . .	23.57	39.13	32.55	1.24	3.51	51.19	52.50	0.67	4.42	88.96
American (red) . .	28.63	38.24	29.64	—	4.49	53.57	52.12	0.72	4.26	89.66
American (pale) . .	31.55	35.93	28.83	0.27	3.12	52.49	53.34	0.82	4.81	88.49
Roquefort . . .	32.26	34.38	27.16	1.32	4.88	50.75	54.24	3.04	4.91	88.70
Gorgonzola . . .	31.85	34.34	27.88	1.35	4.58	20.39	53.08	2.11	4.40	89.18
Cheddar (medium) .	35.60	31.57	28.16	0.45	4.22	49.02	50.49	1.43	4.55	88.75
Gruyère . . .	33.66	30.69	30.67	0.27	4.71	46.26	47.07	0.81	4.41	88.97
Cheshire . . .	37.11	30.68	26.93	0.86	4.42	48.78	50.84	1.69	5.55	87.76
Single Gloucester .	35.75	28.35	31.10	0.31	4.49	44.12	45.24	1.28	6.68	86.89
Dutch . . .	41.30	22.78	28.25	0.57	7.10	38.80	42.41	4.45	5.84	87.58

The ripening process in cheese whereby it usually acquires a more agreeable flavour is essentially a fermentation of a slow character. The amount of water decreases as ripening proceeds, but the percentage of fat is not perceptibly altered nor the total amount of nitrogen, although the albuminoids become gradually soluble, being converted into *caseo-glutin*, a substance soluble in hot alcohol, which appears to be identical with Ritthausen's glutin: hence we may conclude that although ripe cheese is more

digestible, it has lost some of its nutritious matter.

**Oleomargarine and Lard Cheese.** The success attending the sale of margarine as a substitute for butter has led manufacturers, especially in America, to introduce foreign fats of animal or vegetable origin in the production of cheese as a means of utilising skim-milk; the cream which has been abstracted being replaced by lard, oleomargarine, and by cotton-seed oil.

## Analyses of Oleomargarine and Lard Cheeses (Bell).

	100 parts of cheese contain				Per cent. of salt	100 parts of fat contain		Melting point of fat
	Water	Fat	Casein and free acids	Ash		Insoluble fatty acids	Soluble fatty acids	
Oleomargarine . . .	30.95	28.80	36.27	3.98	1.14	92.43	2.16	77°F.
Lard . . .	31.30	24.66	38.87	5.17	1.55	92.88	1.55	92°F.

In flavour and character these samples closely resembled milk-fat cheese. Comparison of the results of the analysis of the two samples with those yielded by genuine cheeses in the former table conclusively proves the admixture with foreign fat. The low percentage of soluble acids indicates that more than one-half of the fat has not been derived from milk. The blue and red moulds which attack cheese are vegetable fungi; the former belonging to the species termed *Penicillium glaucum*, while the latter has been called *Sporendonema casei*, but is probably not autonomous. The cheese-maggot is the larva of the fly *Piophilus casei*; the cheese-mite is *Acarus siro*.

**CHELENTITE.** A mineral from Schneeburg.

As. S. Bi. Ca. Fe. Co. Ni. In-ol. Sp.gr.  
 7.14 1.31 0.66 1.65 5.10 12.66 3.02 0.32=99.86 6.3  
 75.05 1.30 0.90 1.52 5.23 12.27 3.00 0.52=99.79 —  
 75.00 1.32 — 1.60 5.22 12.61 3.05 —=99.80 —  
 (L. W. McCay, Z. K. 9, 606).

**CHEDEVIXITE.** A mineral from the American Eagle Mine, Tintic Mining District, Utah, containing:

As<sub>2</sub>O<sub>3</sub>. CuO. CaO. MgO. Fe<sub>2</sub>O<sub>3</sub>. Al<sub>2</sub>O<sub>3</sub>. H<sub>2</sub>O. SiO<sub>2</sub>.  
 35.14 26.31 0.44 0.16 27.37 0.66 9.33 0.40=99.81  
 Hardness 3.5 (Hillebrand, C. J. 50, 517 Z. 11, 286).

**CHERRY LAUREL, OIL OF, v. OILS, ESSENTIAL.**

**CHERRY TREE GUM v. GUMS.**

**CHERT.** *Feuerstein*, *Hornstein*, Ger. A silicious mineral allied to chalcedony and flint. Similar terms are applied to hornstone and to any impure flinty rock, including the jaspers. It is worked extensively from carboniferous limestone quarries in Flintshire, especially at Halkin and Talaere. It is used in potteries for paving the mills in which flints are ground. The following is an analysis of a sample from Vizzini, Sicily, given by Ricciardi (G. 11, 319):—

Interior					
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	CaO	H <sub>2</sub> O	S.G. at 22°
95.31	0.30	0.25	0.47	2.81=100.14	2.572

White crust metamorphosed by heat

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	CaO	H <sub>2</sub> O	S.G. at 22°
97.02	0.32	3.39	0.55	1.68=102.96	2.520

**CHESSYLITE or CHESSY COPPER.** *Kupferlasur*, Ger. A blue carbonate of copper found native at Chessy, near Lyons (v. COPPER).

**CHIAN TURPENTINE v. OLEO-RESINS.**

**CHICORY.** The plant *Cichorium Intybus*, nat. ord. *Compositæ*; the name is an Anglicised French word, the original being *chicorée*. It is indigenous to England where it is commonly known as wild succory; and in its cultivated

state it is also found there; but is obtained in larger quantities from Holland and Belgium. The roasted root was very extensively used as an adulterant to coffee, the legislature finally requiring that its mixture with coffee must be notified to the purchaser. It is entirely destitute of the properties which render coffee an agreeable and nerve-stimulating beverage, while on the other hand it possesses medicinal properties of a diuretic and laxative character which render its excessive use deleterious. In its preparation, the root is cut in slices of half an inch in length; dried in a kiln; and subsequently roasted as required in the same way as coffee; and finally ground. About 2 lbs. of lard is added to each hundredweight of the root during roasting either to induce a resemblance to coffee or to render the powder less hygroscopic.

**CHILI SALTPETRE.** *Sodium nitrate*, v. SODIUM.

**CHINA BLUE.** Syn. *Water Blue*, *Cotton Blue*, *Opal Blue*, v. TRIPHENYL METHANE COLOURING MATTERS.

**CHINA CLAY or KAOLIN** v. CLAY.

**CHINA GRASS.** *Rhea Ramie fibre*. This substance is the fibre of two (or perhaps more) species of the genus *Boehmeria*, nat. ord. *Urticaceae*, shrubs allied to the nettle (*Urtica*), but possessing no stings, namely, *Boehmeria nivea* or *Urtica nivea* with a white underleaf, and *B. utilis* with a green underleaf. It is the Tchou-ma of China and the Rhea of Assam. The plants grow to a height of from three to five feet, throwing up numerous straight shoots as thick as the little finger and covered with short soft hairs. Its leaves grow upon long foot-stalks and are broadly heart-shaped, about six inches long by four broad. It is a native of China and Sumatra, where, as in India, it has long been cultivated.

Its manufacture into mats used for making sails, foot-mats, &c., is carried on in Southern China, where three crops of Tchou-ma are taken each year, of which the second is the best. For this purpose the grass is sorted into bundles, which are soaked in water for two or three days and then dried in the sun. If a red colour is desired the grass is steeped in a decoction of sapan wood, if yellow in a decoction of the seeds and flowers of the common Chinese plant *mi-fa* or in one of *Sophora japonica*, to which a little alum is added as a mordant. Other vegetable dyes are also employed; but of late years aniline colours have in a measure taken their place.

By processes of manufacture an exceedingly fine fibre is produced on separating the filaments of the stalk, a fibre distinguished by its strength, which is nearly three times that of Russian hemp, by its length, which is greater than that of any bast product, and by its lustrous, silky appearance. Great efforts have been made, with more or less success, to render the use of the fibre in European textile manufactures commercially profitable. It will be seen from the following remarks that there are difficulties in the way. In the first place the method of separating the bast by hand was tedious, and could only be performed whilst the stems were quite fresh, thus limiting its production to the immediate neighbourhood of the plant's growth: In China

the bark is stripped from the stems and the fibre scraped off with a knife, a process which removes the whole so-called grass if performed while the stem is still quite fresh, but leaves a large portion if it has become at all dry. Even under the best conditions a very skilful operator can collect only two pounds of grass per day, the average quantity obtained being only half a pound to one pound. It is further found that owing to the large amount of pectinic substances contained in these *urticaceae*, the long steeping or retting processes used with flax and hemp cannot be practised on account of the ensuing excessive fermentation, which injures the fibre. Experiments made in India with unskilled workers gave about four ounces per day each as the result of their labour. Attention has consequently been given to mechanical processes for separating the fibres from the bark in the green and in the dry state. With this in view the India Office some years ago submitted samples of the dried article to Dr. Forbes Watson, who reported that he did not find it at all difficult to obtain the fibre from stems which were quite dry. The difficulty in the case of India is that the best crops are obtained during the rainy season, when it is all but impossible to dry the stems except by expensive artificial means; while, as above pointed out, the liability of the plant to ferment resulted in the spoiling of the crops when its treatment was delayed. The Government of India has followed up its inquiries and encouraged inventors to competition in producing a machine capable of dealing with the green crop. It may be said that this encouragement has resulted in an approximation to success; thus, in one instance of a machine consisting of a cylinder with beaters revolving at a high speed against the stems upon which meanwhile a jet of water is poured, Dr. Watson estimated the cost of producing the fibre to average 4*l.* to 5*l.* per ton. The yield from the machine was from 1 to 2 tons of green stalks per day, estimated to produce about 100 lbs. of cleaned fibre.

In the treatment of green stalks by hand the Favier's process consists in subjecting the plants to the action of steam for fifteen to thirty minutes, after which the bark is easily stripped. Those stems also which have been standing some time after being cut can also be treated without leaving any appreciable amount of fibre on the stalks.

The operation of scutching the dried stems presents no difficulty when steam power is applicable and when the quantity of material to be treated is sufficiently large. The next process, however, of 'ungumming' has given a little trouble. Since China grass contains from 22 to 28 or, in some cases, up to 35 p.e. of gum; it is necessary to remove this constituent of the fibre before it can be spun into yarn. For this purpose many partly mechanical and partly chemical processes have been devised. It may sufficiently describe the lines which these various systems take to say that they resemble generally the processes adopted in the scouring and bleaching of cotton goods—that is to say, by subjecting the material to pressure under the application of steam, and to alternate treatment of alkaline and acid agents.



China grass has little or no attraction for dyes, and consequently the methods adopted in the dyeing of cotton or of jute are applicable to it. It is found that mineral colours, such as chrome yellow and orange, destroy the peculiar lustre of china grass; the yellow dye obtained with cadmium sulphide, however, is not open to this objection. Alizarine mordanted with Turkey red oil destroys the lustre, whilst aniline colours fixed with the same mordant do not. Rosaniline derivatives and azo-colouring matters may be used satisfactorily. It is recommended that the grass should be dyed immediately after retting and before spinning to preserve the characteristic sheen.

The textiles formerly associated with China grass were such articles as handkerchiefs and 'grass cloths,' imported direct from China; but under the influence of recent efforts to introduce the manufacture as well as the growth of China grass into Europe, other developments must be noted. Thus at the manufactory of Zittan, in Saxony, the fibre has already found extensive application in tapestry and dress goods, table-cloths, damasks, lace, fancy knitting yarns, &c.

#### CHINA INK v. INDIAN INK.

**CHINA STONE.** A granitic rock, having its felspathic constituent more or less decomposed, but not completely kaolinised. As the felspar still retains part of its alkali, and as some micaceous mineral is generally present, the stone is fusible; hence it is largely used in the manufacture of porcelain, and when free felspar is not introduced it forms the only vitrifiable constituent of the paste. China stone is sometimes known as 'Cornish stone' in consequence of its being largely worked in Cornwall, where it was discovered by W. Cookworthy, of Plymouth, about 1759. He first noticed it at Tregomming Hill, near Breague, and described it under the local name of 'growan' or 'moor stone.' It is now obtained principally from the neighbourhood of St. Stephens, near St. Austell. The rock requires no preparation, but is sent direct from the quarry to the potteries. Notwithstanding the altered condition of the felspar, it is used locally as a building stone, and found to be durable.

The conditions under which the china stone has been formed are obscure. Its occurrence sometimes in narrow bands, and its altered character at great depths, render it improbable that the decomposition has been due to the superficial action of meteoric agents, such as water and carbon dioxide. Daubrée, Smyth, Le Neve Foster, Collins, and other observers in Cornwall have held that the granite has been decomposed probably by means of compounds containing fluorine rising from below; a view supported by the fact that the china stone and kaolin occur in association with veins of tin ore and various fluorine-bearing minerals (Daubrée, *Géol. expér.* 1879, p. 64).

Cornish stone consists usually of quartz, altered orthoclase, and gilbertite; frequently associated with lepidolite, or lithia-mica, known to the Cornish quarrymen as 'shell,' and occasionally with schorl, or black tourmaline, and fluor-spar as accessory constituents. The gilbertite (hydrated silicate of aluminium and potassium) seems to have been mistaken by some observers for tale (hydrated silicate of magnesium),

as the china stone has been frequently described as an altered talcose granite. The following analyses of the china stone of St. Stephens, Cornwall, were made by J. B. Hannay, and are given by J. H. Collins (*Hensbarrow Granite District, Truro, 1876, p. 31*):

Silica . . . . .	73.39	69.50	71.66
Alumina . . . . .	16.50	17.85	18.79
Limo . . . . .	0.50	2.66	1.70
Magnesia . . . . .	0.31	0.12	0.35
Potash (with a little soda) . . . . .	7.66	7.98	6.60
Iron . . . . .	trace	trace	trace
Manganese . . . . .	—	trace	trace
Fluorine . . . . .	0.74	0.71	0.14
Water . . . . .	1.25	1.30	0.91

100.35 100.12 100.15

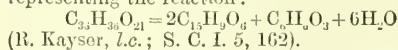
It has been proposed by Collins to distinguish china stone under the name *Petunzite*, a word suggested by the Chinese *pe-tun-tse*. In the early part of the last century a Jesuit missionary named D'Entrecolles residing at King-te-chin, sent to Réaumur, in Paris, samples of the raw materials used in China. These were the first specimens of their kind that had ever reached Europe, and they led to the foundation of the manufacture of porcelain at Sèvres. The china stone was described by D'Entrecolles as *pe-tun-tse*, and the china clay as *kaolin*; but it appears that the former name, if not both, must have been erroneously applied. According to the Chinese scholar, Stanislas Julien (*Hist. et Fabric. de la Porcel. Chin., Paris, 1856, preface p. xx*), *pe-tun* signifies 'white paste,' while *tse* is merely a diminutive applied to the material when worked up into small cakes. Hence, *pe-tun-tse* is really the name of small blocks of white clay or prepared paste, and not of the granitic rock. Nevertheless, custom in this country has justified the use of the term *pe-tun-tse* as synonymous with china stone. F. W. R.

**CHINESE BLUE** (*Porzellanblau*, Ger.). Several compounds are sold under this name, of which the following are examples; ultramarine and flake white; cobalt blue and white lead; and a double cyanide of iron (Prussian blue), v. **PIGMENTS**.

**CHINESE GREEN** or **LOKAO**. This colouring matter is obtained in China from different varieties of buckthorn (*Rhamnus*), and is brought into commerce in the form of thin blue slabs, easily broken, but difficult to pulverise. It is a lake containing the colouring matter lokain, with from 26 p.c. (Cloeze and Guignot, B. 5, 338) to 47 p.c. of clay and chalk (Kayser, B. 18, 3417). To obtain the pure colouring matter lokao is extracted with ammonium carbonate solution; on the addition of alcohol to the filtrate, a deep blue precipitate of the ammonia compound of lokain  $C_{12}H_{18}O_{27}$  is formed. From the solution of this compound in water, oxalic acid precipitates lokain, which, when dried, is a pulverulent bluish-black substance insoluble in water, alcohol, ether, chloroform, and benzene. Friction imparts to it metallic lustre. The monammonium salt forms small crystals with bronze-like lustre, from which the diammonium salt  $C_{12}H_{16}O_{27}(NH_4)_2$  is obtained by moistening them with ammonia and subsequent drying over sulphuric acid. The barium salt  $C_{12}H_{16}O_{27}Ba$  is insoluble in water and alcohol. The potassium

salt  $C_{12}H_{16}K_2O_{22}$  forms a dark-blue amorphous precipitate from alcohol. Soluble compounds of lokain show perfect absorption of the spectrum in the red and yellow portions only. Boiling dilute acids decompose lokain into a carbohydrate lokaose  $C_6H_{12}O_6$ , and lokanic acid  $C_{10}H_{16}O_{21}$ ; the latter is a bluish-violet crystalline powder insoluble in water, alcohol, and ether, containing 1 molecule of water, which is given off at  $120^\circ$ . The ammonium salt  $C_{10}H_{16}O_{21}NH_4$  is a deep-blue powder soluble in water, with a violet colour; the barium and lead salts are dark-blue powders insoluble in water and alcohol. Soluble compounds of lokain in very dilute solution show a characteristic perfect absorption in the yellow and yellow-green portions of the spectrum. Lokaose reduces Fehling's solution with half the power of glucose, from which it also differs by its optical inactivity. The decomposition of the lokain is expressed by the equation  $C_{12}H_{16}O_{22} = C_6H_{12}O_6 + C_{10}H_{16}O_{21}$ . Reducing agents convert blue solutions of lokain and lokanic acids into blood-red solutions, which become green on exposure to the air.

Lokanic acid is decomposed by cold concentrated sulphuric acid according to the equation  $C_{10}H_{16}O_{21} - 5H_2O = C_4H_8O_{16}$ . This latter substance forms a red-brown powder; its barium compound  $C_4H_8BaO_{16}$  is also a red-brown substance. Concentrated potash solution (50 p.c.) decomposes lokanic acid into a brown powder and phloroglucinol; the former body is termed delokanic acid  $C_{12}H_{16}O_{21}$ , the following equation representing the reaction:



(R. Kayser, *l.c.*; S. C. I. 5, 162).

**CHINESE LAKE** or **SCARLET LAKE** v. PIGMENTS.

**CHINESE TALLOW.** A white vegetable tallow covering the seeds of *Stillingia sebifera*, used for candle-making.

**CHINESE WAX** v. WAX.

**CHINESE YELLOW** (*King's yellow*) v. PIGMENTS.

**CHINOLINE** v. QUINOLINE.

**CHINOLINE BLUE** v. QUINOLINE BLUE.

**CHIOLITE.** A double fluoride of aluminium and sodium  $3AlF_3 \cdot 5NaF$  closely akin to cryolite  $AlF_3 \cdot 3NaF$ . Found at Minsk (Brandl, J. M. 1882; 2nd Ref. 201; C. J. 44, 29).

The following analysis is given by Brandl (A. 213, 1):

Al	Na	F
17.66	24.97	57.30 = 99.93
17.64	25.00	57.30 = 99.94

**CHITIN** v. GLUCOSIDES.

**CHLOANTHITE.** A mineral from Schneeberg containing

As	S	Bi	Fe	Cu	Ni
68.40	1.06	0.21	0.69	4.20	21.95 = 99.51

Sp.gr. 6.44 (J. 37, 1901).

**CHLORAL** *Trichloroacetaldehyde*  $CCl_3 \cdot CHO$ .

Chloral was first prepared by Liebig, who obtained it by the continuous chlorination of absolute alcohol (A. 1, 189). It was further examined by Dumas (A. Ch. [2] 56, 125), who determined its composition, and by Städeler (A. 61, 101). Although a chlorinated aldehyde, it cannot be prepared by treating acetaldehyde with chlorine, unless water is present together with calcium carbonate to neutralise the hydro-

gen chloride formed, since butyric chloral results when dry materials are employed (Pinner, B. 4, 256).

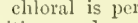
**Preparation.**—Absolute alcohol is treated continuously with dry chlorine in the cold, care being taken to avoid a rise of temperature at first; afterwards, when the absorption of the gas diminishes, the temperature of the alcohol is gradually raised to about  $60^\circ$ , and the current continued until the action is complete and chlorine is no longer absorbed by the syrupy liquid. In this reaction chloral alcoholate is formed, and on digestion at  $60^\circ$  for several hours with twice its volume of strong sulphuric acid this is decomposed into alcohol and chloral, the latter of which separates as an oil and can be purified by distillation over calcium carbonate. Ethylene dichloride, ethylidene chloride, and chlorinated ethylene dichloride (b.p. =  $115^\circ$ ) are also formed as by-products in this reaction (Krämer, B. 3, 257). According to Page (A. 225, 209) the chlorination proceeds more rapidly, and the yield of chloral is greater if a small percentage of ferrie chloride is previously added to the alcohol; ethyl chloride is produced in the reaction, and instead of the alcoholate a mixture of chloral and chloral hydrate results.

Theories to explain the formation of ehloral have been proposed by Lieben (B. 3, 910), and by Wurtz and Vogt (C. R. 71, 777; compare also Jacobsen, B. 15, 601).

**Properties.**—Chloral is a colourless pungent liquid, which solidifies at  $-75^\circ$  (Berthelot, Bl. 29, 3), and is readily soluble in water, alcohol, and ether. Its b.p. =  $97.7^\circ$  (cor.) and sp.gr. = 1.54175 at  $0^\circ$  (Passavant, C. J. 39, 55; Thorpe, C. J. 37, 191); b.p. =  $96^\circ$ – $97^\circ$  at 750 mm., and sp.gr. = 1.5121 at  $\frac{20^\circ}{4^\circ}$  (Brühl, A. 203, 11). Nascent hydrogen reduces it to aldehyde (Personne, A. 157, 113), which it closely resembles in reducing ammoniacal silver nitrate solution (Städeler, A. 106, 253), and in forming crystalline compounds with alkaline bisulphites (*ibid.*); with ammonia (Personne, *l.c.*; C. R. 71, 228); with hydrogen cyanide (Bischoff and Pinner, B. 5, 113; A. 179, 77); and with amides and amines (Wallach, B. 5, 251). When heated with aqueous alkalis it decomposes into chloroform and an alkaline formate, and a similar reaction occurs when alcoholic potash or soda is employed (Kekulé, A. 119, 188). Fuming nitric acid converts it into trichloroacetic acid, and, according to Grabowski (B. 6, 225), fuming sulphuric acid combines with it in the cold, but on heating converts it into chloralide  $C_2H_3Cl_3O_3$  (compare Grabowski, B. 8, 1433; Städeler, A. 61, 114; Wallach, A. 193, 1).

When pure, chloral is perfectly stable, but traces of impurities, and particularly of sulphuric acid (Byasson, C. R. 91, 1071) convert it into *metachloral*—a white amorphous substance insoluble in water, alcohol, and ether—which, on distillation at  $180^\circ$ – $250^\circ$ , is recovered into ordinary chloral (Kolbe, A. 54, 183 [footnote]).

**Chloral hydrate**  $CCl_3 \cdot CH(OH)_2$  or



is formed by dissolving chloral in water. On the manufacturing scale it is prepared, according to Detschnyi (D. P. J. 209, 224, with figure) by passing chlorine into alcohol of at least 96 p.c.

When 120–150 lbs. of alcohol are employed the current must be maintained for 12–14 days, during which time the temperature rises to 60–70°, and the product acquires a density of 41°B. The crude product so obtained is purified by heating it with an equal weight of concentrated sulphuric acid in copper vessels lined with lead. Considerable quantities of hydrochloric acid escape at first, and when the evolution has ceased the product is distilled, chloral passing over in the fraction 95–100°. This is redistilled in similar vessels, and the distillate mixed with the requisite quantity of water; the hydrate is then either allowed to solidify in cakes or is poured into vessels one-third filled with chloroform, to crystallise. It may be crystallised with advantage from carbon bisulphide or turpentine (Flückiger, Z. [2] 6, 432).

*Properties.*—Chloral hydrate crystallises in monoclinic tables (Groth, B. 5, 676), and has a peculiar odour and sharp taste. Its m.p. = 57° (Meyer and Dulk, A. 171, 75), b.p. = 97·5°, and sp.gr. = 1·818 (in powder) and = 1·818 (crystallised) (Schröder, B. 12, 562). It dissolves readily in water, alcohol, ether, chloroform, turpentine, and light petroleum, and its solubility in carbon bisulphide is given by Flückiger (*l.c.*) as 1 in 45 at 15–18°, and 1 in 4·5 at the boiling-point. Concentrated sulphuric acid decomposes it into chloral and water, and alkalis act upon it as upon chloral. A modification of the hydrate, melting at 80°, is obtained by rapidly evaporating an acetic acid solution of anhydrous chloral over sulphuric acid (Meyer and Dulk, *l.c.*).

*Physiological action.*—Compare Liebreich (B. 2, 269); Personne (C. R. 78, 129); Byasson (C. R. 78, 649); Tomaszewicz (abstracted, C. J. 1874, 814); and Tanret (J. Ph. [4] 20, 355).

*Estimation.*—4 grams of the sample are dissolved in water, and any free acid removed by shaking either with chalk or barium carbonate and filtering. The filtrate is treated with a moderate excess of normal caustic soda solution, and titrated back with normal acid in the usual way, litmus being used as an indicator. Each c.c. of the normal alkali used corresponds to 0·1475 gram of chloral or 0·1665 gram of chloral hydrate (Meyer and Haffter, B. 6, 600).

Another method in which milk of lime is used to effect the decomposition of the chloral has been proposed by Wood (Ph. J. [3] 1, 703).

*Chloral alcoholates.* Chloral combines with absolute alcohol forming *chloral ethylalcoholate*  $\text{CCl}_3\text{CH}(\text{OH})\cdot\text{OEt}$  (Martius and Mendelssohn, B. 3, 444), identical with the final product of the action of chlorine on absolute alcohol (Lieben, B. 3, 907). This crystallises in needles, melts at 44–46° (Meyer and Dulk, A. 171, 78), at 46° (Lieben), boils at 115°, is sparingly soluble in water, and decomposes into chloral and alcohol on treatment with concentrated sulphuric acid. Other alcoholates have been described by Jacobson (A. 157, 244).

*Butyric chloral*  $\text{CH}_3\text{CHCl}\cdot\text{CCl}_2\cdot\text{CHO}$ .

Krämer and Pinner, by passing dry chlorine into acetaldehyde or, preferably, paraldehyde, cooled at first, but afterwards heated at 100°, obtained a compound which was at first regarded as crotonic chloral  $\text{C}_4\text{H}_7\text{Cl}_2\text{O}_2$ , but is now identified as butyric chloral (A. 179, 26; B. 3, 383;

8, 1562). It is a colourless oil, having a characteristic chloral odour, boils at 161°–165° at 750 mm. (Brühl, A. 203, 20), and resembles chloral in forming compounds with water, ammonia, amides and hydrogen cyanide.

**CHLORALUM** *v.* DISINFECTANTS.

**CHLORANIL** *v.* TETRACHLORQUINONE.

**CHLORATE OF POTASH** *v.* CHLORINE.

**CHLORATE OF SODA** *v.* CHLORINE.

**CHLORIDE OF LIME** *v.* CHLORINE.

**CHLORIDE OF POTASH** *v.* CHLORINE.

**CHLORIDE OF SODA** *v.* CHLORINE.

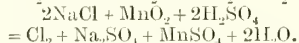
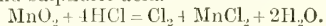
**CHLORINE.** Symbol Cl. At. w. 35·37.

Chlorine was first obtained by Scheele in 1774 by the action of hydrochloric acid upon manganese dioxide, and was termed by him 'dephlogisticated marine acid air.' The idea that it was a compound substance prevailed until 1809, when Gay-Lussac and Thenard suggested that it was probably an elementary body, a supposition confirmed by the investigations of Davy in 1810 (T. 1811, 1, 32). Davy gave it its present name, from *χλωρὸς* greenish-yellow, in allusion to its characteristic colour.

Chlorine is never found free in nature; it exists mainly in combination with sodium, potassium, calcium, magnesium, &c. Sodium chloride occurs as *rock salt* in large quantities in Galicia, Tyrol, Transylvania, Spain, and in England (particularly in Cheshire) (*v.* SODIUM). Potassium chloride is found as *sylvine* (*q. v.*), and in association with magnesium chloride as *carnallite*  $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  (*q. v.*) in the salt beds of Stassfurt. Other naturally occurring chlorides are *matlockite*  $\text{PbCl}_2\cdot\text{PbO}$ , *horn silver*  $\text{AgCl}$ , *atacamite*  $\text{Cu}_2\text{Cl}(\text{OH})_2$ , *calomel*  $\text{HgCl}_2$ , &c. Ferric chloride  $\text{Fe}_2\text{Cl}_6$  and sal ammoniac are occasionally found native as products of volcanic action. Alkaline chlorides are also found in considerable quantity in sea-water and in many natural waters.

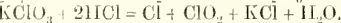
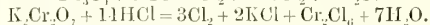
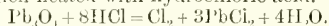
Sodium and potassium chlorides are present in most animal secretions, and free hydrochloric acid is met with in the gastric juice. Many plants, especially those growing in proximity to the sea, contain notable quantities of chlorides.

The readiest mode of preparing chlorine for laboratory purposes consists in heating manganese dioxide with hydrochloric acid, or by heating a mixture of manganese dioxide, common salt, and sulphuric acid.



Both these processes are used on the large scale for the preparation of chlorine (*v. infra*).

Many other peroxides and certain oxysalts may also be used for the preparation of chlorine; thus red lead and potassium bichromate generate the gas when heated with hydrochloric acid.



Chlorine is also formed when the heated vapours of nitric and hydrochloric acid react upon each other:  $2\text{HCl} + 2\text{HNO}_3 = \text{Cl}_2 + \text{N}_2\text{O}_5 + 2\text{H}_2\text{O}$ .

Certain chlorides, *e.g.*  $\text{Mg}_2\text{Cl}_2$  in air,  $\text{PbCl}_2$ ,  $\text{AuCl}_3$ , &c., evolve chlorine when heated.

(For other processes *v. infra*.)

At ordinary temperatures and pressures chlorine is a greenish-yellow gas, which becomes



darker in colour as it is warmed; under strong pressures the colour becomes orange-yellow. Even when largely diluted with air the gas possesses a characteristic pungent and irritating smell; it cannot be respired, as it rapidly attacks the membranes. The gas is incombustible in air, although it may be made to burn in hydrogen; ordinary illuminating flames, e.g. of coal-gas, tallow, wax, &c., burn in chlorine with separation of carbon and formation of hydrochloric acid gas.

The sp.gr. of chlorine shows a gradual diminution up to  $240^{\circ}$ , when its density becomes normal, viz. 2.4502 (Jahns, B. 15, 1238).

$40^{\circ}$	$80^{\circ}$	$120^{\circ}$	$160^{\circ}$	$200^{\circ}$	$240^{\circ}$
2.4844	2.4776	2.4708	2.4641	2.4572	2.4504

The absorption spectrum of chlorine shows numerous dark lines in addition to complete absorption in the blue and violet.

Chlorine is readily liquefied to a dark greenish-yellow liquid of sp.gr. 1.33, b.p.  $33.6^{\circ}$ . It can be solidified at a low temperature. Liquid chlorine is not miscible with water; its refractive index is lower than that of water, and it is a non-conductor of electricity.

Chlorine gas is readily soluble in water, its absorption co-efficient between  $10^{\circ}$  and  $41.5^{\circ}$  according to Schönfeld (A. 93, 26; 96, 8) is

$$3.0361 - 0.046196t + .0001107t^2$$

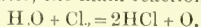
by means of which the following table showing the volume of chlorine at  $0^{\circ}$  and 760 mm. absorbed by 1 vol. of water at varying temperatures is calculated

$10^{\circ}$	$15^{\circ}$	$20^{\circ}$	$25^{\circ}$	$30^{\circ}$	$35^{\circ}$
2.5852	2.3681	2.1565	1.9504	1.7499	1.5550

(v. also Pickering, C. J. 1880, 139).

The volume of chlorine absorbed from a mixture of that gas with an indifferent gas, as hydrogen or carbon dioxide, is greater than that calculated from the law of partial pressures (Roscoe, C. J. 8, 14).

Chlorine-water has the characteristic smell and colour of the gas; in daylight, and especially when exposed to sunshine, it gradually loses its colour owing to the action of the chlorine on the water, the main reaction being



On cooling a saturated solution to  $0^{\circ}$  it deposits crystals of so-called chlorine hydrate of a light yellow colour, which become almost white when cooled to  $-50^{\circ}$ . By gently heating the crystals in a sealed tube they are readily resolved into water and free chloride which may be thus obtained as a liquid.

Chlorine is an active chemical agent, and combines with many substances even at the ordinary temperature. Phosphorus ignites spontaneously in the gas forming phosphorus trichloride, which, in contact with excess of chlorine, is ultimately converted into phosphorus pentachloride. Finely divided arsenic, antimony, copper, tin, lead, and iron burn in chlorine forming the respective chlorides. Certain of these reactions are modified if the chlorine is absolutely free from moisture. Wanklyn (C. N. 20, 271) found that sodium might be melted in dry chlorine without action, although the metal readily burns in chlorine as ordinarily prepared. Cowper (C. J. 43, 153) found that Dutch metal, zinc, and magnesium were unacted

upon by dry chlorine; silver and bismuth were only slowly attacked.

Sulphur dioxide, ethylene, and carbon monoxide readily unite with chlorine. Chlorine rapidly attacks many organic substances forming *addition products* as in the case of ethylene, or *substitution products* as in that of marsh gas. Chlorine has, indeed, a very strong affinity for hydrogen; a lighted taper plunged into an atmosphere of chlorine continues to burn with a dull lurid flame accompanied by much soot. If a piece of paper moistened with oil of turpentine  $\text{C}_{10}\text{H}_{16}$  be thrust into a jar of the gas, it takes fire and burns with a cloud of smoke. By reason of its tendency to unite with hydrogen chlorine acts indirectly as an oxidising agent in presence of moisture. Many metallic protoxides are converted into peroxides by the action of the gas in presence of water, the hydrogen of which combines with the chlorine to form hydrochloric acid, whilst the liberated oxygen attacks the metallic oxide. If a stream of chlorine is led into an alkaline solution containing sulphur, or a sulphur compound in solution or suspension, the sulphur, in presence of water, is rapidly oxidised by the nascent oxygen to the state of sulphuric acid. The oxidising action of chlorine is frequently made use of in chemical analysis. By virtue of its oxidising action chlorine destroys many organic colouring matters, and is hence used directly or indirectly for bleaching. It is also used as a disinfectant.

#### INDUSTRIAL PREPARATION OF CHLORINE.

Chlorine is always prepared by the action of hydrochloric acid on substances capable of oxidising the hydrogen, thus setting the chlorine at liberty. The hydrochloric acid is nearly always employed in the free state, as it is obtained in the technical process of manufacturing sodium sulphate by decomposing common salt by sulphuric acid. But sometimes local circumstances still compel the direct use of a mixture of sodium chloride and sulphuric acid with manganese peroxide even for manufacturing purposes; and recently a large number of proposals have been made for manufacturing chlorine from hydrochloric acid in the nascent state as it is by suitable means obtained from magnesium chloride or other chlorides.

The substance which supplies the 'active' oxygen for liberating chlorine from hydrochloric acid is nearly always manganese dioxide, either in the native state or artificially prepared by atmospheric oxygen from the residual liquors of the chlorine process (Weldon mud, v. *infra*). There are, however, processes for employing atmospheric oxygen directly for that purpose, one of which, the Deacon process, has been practised on a large scale for many years past, while others, such as the Péchiney-Weldon process, cannot as yet be said to have passed the experimental stage.

#### RAW MATERIALS FOR THE MANUFACTURE OF CHLORINE.

1. Hydrochloric acid (technically also called *Muriatic acid*).

The solution of hydrochloric acid used for the manufacture of chlorine ought to be as

strong as possible, especially if employed with native manganese ore, as dilute acid, or that which has been neutralised to a certain extent, acts too slowly, even at higher temperatures. Suppose that this limit is reached at 6 p.e. HCl, it is evident that much more is utilised of 33 p.e. than of 20 p.e. acid, namely, in the first case  $33 - 6 = 27$ , or  $\frac{27}{33} = 82$  p.e. of the total HCl; in the second case  $20 - 6 = 14$ , or  $\frac{14}{33} = 70$  p.e. of the total HCl. Usually the free acid left in the still liquors from native manganese amounts to much more than that, thus making a much greater difference between more or less highly concentrated acid.

When working with recovered manganese (Weldon mud), the difference is not so striking, but it still exists, and the greater dilution of the liquors caused by the employment of weak acid is also a serious drawback. Hydrochloric acid below 20° Tw. = 20 p.e. HCl ought never to be employed for chlorine making. It is quite evident that the yield of chlorine from a given quantity of salt must be greater if the hydrochloric acid is employed in a concentrated state than *vice versa*.

In the Deacon process the hydrochloric acid is used as gas, and as it comes from the decomposing pots. The roaster acid is not used in this process, because it is too much diluted with air and is too impure (*v. infra*).

The impurities of hydrochloric acid are usually of no consequence; but that which is employed for decomposing Weldon mud ought to be as free from sulphuric acid as possible, because the latter acid forms calcium sulphate with the calcium chloride present in the mud, which greatly increases the quantity of deposit in the neutralising wells, and causes a loss of manganese unless specially treated. In the Deacon process the presence of sulphuric acid in the gaseous hydrochloric acid is even more objectionable. The hydrochloric acid from the pots contains much less sulphuric acid than that from the roasters, and in the Deacon process only the former can be used, the roaster-acid being worked up according to Weldon.

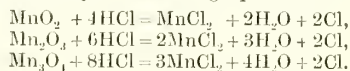
It has been proposed to purify the hydrochloric acid from sulphuric acid by adding calcium chloride (Weldon and Strype, E. P. 222, 1881) or barium chloride (Wigg, E. P. 1220, 1882) to it. In the latter case the BaSO<sub>4</sub> may be converted into BaCl<sub>2</sub> by furnacing with CaCl<sub>2</sub>, or else it may be used as a paint (as 'permanent white').

2. **Sodium chloride** (common salt) along with sulphuric acid is sometimes used for making chlorine at bleach works, &c., where local circumstances cause this process to be cheaper than the use of hydrochloric acid (*v. infra*).

3. **Calcium chloride and magnesium chloride**, as they are produced in the manufacture of alkali by the ammonia process, in working up the mother liquors from the manufacture of sea-salt, and in the mother liquors from the Stassfurt potassium chloride &c., are the subject of many proposals for extracting chlorine, the more important of which will be noticed hereafter.

4. **Manganese ore** was formerly the only substance practically employed for liberating Cl from HCl, and is even now indispensable, to a certain extent, for making up the losses of manganese in

the Weldon process, and in all cases where the manufacture of chlorine is carried on in a comparatively small way, so that the modern processes for its production do not pay. Only such manganese ores are available for this purpose as contain a somewhat considerable quantity of 'active oxygen' in the shape of MnO<sub>2</sub>. The lower oxides of manganese also yield chlorine as far as they contain more oxygen than MnO; but they consume too much acid for this purpose, as will be seen by the following equations:



The following ores of manganese are the most important:

**Pyrolusite** MnO<sub>2</sub>. It crystallises in rhombic prisms, but is mostly found in indistinctly crystalline masses of a fibrous structure. Its sp.gr. is 4.7-5.0; its colour is dark steel-grey to light iron-grey, with semi-metallic lustre. It is very soft and soils the fingers, but there is also a hard variety of MnO<sub>2</sub>, called *polianite*.

**Braunite** Mn<sub>2</sub>O<sub>3</sub> is mostly found associated with pyrolusite. It is generally indistinctly crystalline, of iron-black or brownish-black colour, and does not soil the fingers, being almost as hard as feldspar. Sp.gr. 4.8-4.9.

**Brown manganese ore (Manganite)** Mn<sub>2</sub>O<sub>3</sub>, 2H<sub>2</sub>O. Sp.gr. 4.3-4.4. Hardness between pyrolusite and braunite. Colour similar to braunite, but fracture brown, whilst that of braunite and pyrolusite is black.

**Hausmannite** Mn<sub>3</sub>O<sub>4</sub>. Sp.gr. 7.8. Colour and fracture similar to the preceding, but has more metallic lustre.

**Psilomelane** generally occurs in kidney-shaped and other forms of a shelly, rarely of a fibrous, structure.

Its composition is complicated; its powder imparts a red colour to concentrated sulphuric acid. Colour, iron- or blue-black; fracture, brownish-black; hardness, considerable. Sp.gr. 4.1-4.2.

Wad is chemically similar to the preceding ore, but is very soft and porous, so that it is very easily acted upon by HCl. Sp.gr. 2.3-3.7. Brown to brownish-black. It is probably the product of decomposition of other manganese ores, and is very important for practical purposes.

Analyses of the various manganese ores are given in Lunge's Sulphuric Acid and Alkali, 3, 115-119. More recent analyses are given by Lill and Schneider (S. C. I. 1883, 411).

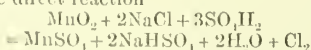
Formerly the manganese ore for chlorine-making (technically called 'manganese') came principally from central Germany. The mines of Ilmenau and Elgersburg even now yield very fine pyrolusite, such as is used by glass-makers; those near Giessen, in the Nassau and Siegen country, were, however, quantitatively much more important for chlorine-making. This 'German manganese' is very soft and, even after washing at the mines, rarely contains much more than 60 p.e. MnO<sub>2</sub>. This, as well as the French manganese (from Romanèche, in the Saône-et-Loire Department), has lost most of its importance since the development of the mines in the Huéla District, which yield manganese ore from 70 to upwards of 85 p.e. MnO<sub>2</sub>.

A considerable quantity of rich ore now comes from Chili. These mines now supply nearly all the requirements of the chemical trade. Other beds have been discovered in the north of Spain, in the north of Italy, in New Zealand, Cuba, West Virginia, &c., but since the consumption of manganese has been very much restricted by the recent progress of chlorine-making, most of the beds do not pay for working. For the analytical methods for testing manganese ore *v. MANGANESE*. They show in the first instance its percentage of active oxygen, that is, the oxygen present over and above that necessary to form  $\text{MnO}$ , which is the only oxygen capable of evolving chlorine from  $\text{HCl}$ . This percentage is, however, expressed in terms of manganese dioxide  $\text{MnO}_2$ . As shown above, the lower oxides of manganese require much more hydrochloric acid to furnish the same quantity of chlorine; more acid may be taken up by iron oxides, alkaline earths, alkalis, &c., occurring in the ore. Even the insoluble matters, as barium sulphate, silica, or silicates, are frequently injurious because they mechanically obstruct the action of  $\text{HCl}$  and may cause a considerable quantity of  $\text{MnO}_2$  to be protected against the acid by a coating of silica &c. Hence the value of manganese ore is not directly proportionate to its percentage of  $\text{MnO}_2$ , but the  $\text{MnO}_2$  is valued more highly the higher the percentage. The custom of the trade is to assume a normal strength of 70 p.e.  $\text{MnO}_2$ , and to add or deduct so much pro p.e. up or down, with a maximum of 65 p.e.  $\text{MnO}_2$ .

Special attention must be paid in testing to the presence of carbonates ( $\text{CaCO}_3$ ,  $\text{BaCO}_3$ , &c.). These not merely waste hydrochloric acid, but the carbonic acid is most objectionable in the manufacture of bleaching powder. Ores containing upwards of 1 p.e.  $\text{CO}_2$  are not considered merchantable; they can, however, be sufficiently deprived of carbonates by crushing and treating with dilute acids.

The physical state of the manganese ore is also of importance. The soft varieties are preferred to the hard ones because they are more easily dissolved and require less acid and steam than the latter.

*The manufacture of chlorine from common salt, sulphuric acid, and manganese ore.*—This is still sometimes carried out in countries where there is no manufacture of hydrochloric acid; this acid, both on account of its much lower concentration and of the greater difficulty of carriage, may then cost much more for its real chemical equivalent than a corresponding quantity of sulphuric acid. Where, therefore, in such cases, chlorine must be produced for bleaching, for the manufacture of fine chemicals, &c., the direct reaction



is employed. It would not be practicable to employ only sufficient acid to form  $\text{Na}_2\text{SO}_4$ , and there must be even an excess of sulphuric acid above that shown in the reaction (corresponding to 87  $\text{MnO}_2$ , 117  $\text{NaCl}$  and 297  $\text{SO}_3\text{H}_2$ ), if the other materials are to be fully utilised.

Usually equal parts of manganese ore and common salt are ground up together, and are charged into a leaden or stoneware still, some-

times provided with a mechanical agitator. The requisite quantity of sulphuric acid, previously diluted with its own volume of water, is gradually added by means of a funnel-tube, and heat is applied, preferably from without, by means of a steam-jacket, till nearly all the chlorine has been evolved. The residue remaining in the still is practically worthless.

There are also systems of stills where the decomposition of  $\text{NaCl}$  by  $\text{SO}_3\text{H}_2$  is carried on separately from that of  $\text{MnO}_2$ , by the  $\text{HCl}$  formed in the first part of the process, but these present no great advantages over the direct mixture of the materials, unless the first operation is carried on as an independent manufacturing operation on the large scale, as in the manufacture of sulphate of soda or 'salteake.'

*The manufacture of chlorine from manganese and liquid hydrochloric acid* is carried out either in vessels made of stoneware, or in stills made of acid-proof natural stone. Stoneware stills can be made only of moderate size, and hence are mostly used for producing chlorine on a medium scale, not for manufacturing bleaching powder; but even for the latter purpose they were preferred by some of the largest French works, so long as they employed only native manganese, owing to their cleanliness and the more thorough utilisation of the acid. In most cases where chlorine is employed for bleaching or for manufacturing fine chemicals, and where this is done with native manganese (as must be the case outside of alkali works) such stills are to be recommended. Fig. 1 shows one of the

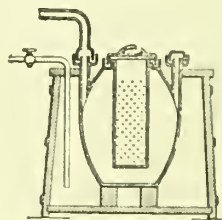


FIG. 1.

best-known forms of stoneware stills, intended for heating from the outside in a water or steam-bath, made of wood or masonry. The manganese is placed into the perforated cylinder, which holds about 1 cwt., and is put in and out by means of specially shaped tongs, through the large opening. The small necks serve for introducing the acid and taking away the gas. At the end of the operation the still-liquor is drawn off by a syphon, or by a discharge-pipe passing through the steam-jacket. Since the acid is not diluted by steam-water, it is much better exhausted than in the large stone-stills described below. Such small stills permit of careful and economical working, so far as materials are concerned, and they necessitate hardly more labour than large ones.

These stoneware stills are sometimes heated by blowing steam into them, but this plan cannot be recommended, as the above-mentioned advantage is thus sacrificed, and, moreover, such stills easily crack.

Another description of small chlorine stills, shown in fig. 2, has been found very efficient,



and is not so liable to give trouble by cracking as those generally used. There is a stoneware cylinder open at the top, with a sieve for holding the manganese and an outlet pipe closed by an indiarubber tube and clamp. This cylinder is covered by a lead (or stoneware) bell, which reaches nearly down to its bottom. This bell

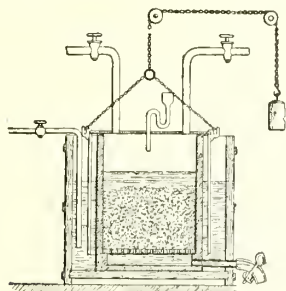


FIG. 2.

can be raised or lowered by means of pulleys and balance weights; it is provided at the top with an acid funnel and two gas-outlets, one of which serves for the ordinary work, whilst the other one serves to carry off the gas in case of an interruption of the former. These gas-pipes are coupled with their continuations in such a way that they can be easily disconnected when the bell is raised for re-charging the stills. The whole is immersed in a wooden tub, partly filled with water which serves as an hydraulic lute; but it is best to provide the rim of the inner cylinder with an india-rubber ring, upon which the top of the lead bell rests, so that there is hardly any communication between the gas-space and the water in the tub. The latter is heated to the proper point by a steam-pipe dipping into it, so that it serves as a water-bath, and, being very hot, it can absorb next to no chlorine from the still.

Fig. 3 shows a contrivance which allows of instantly connecting or disconnecting the chlor-

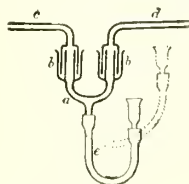


FIG. 3.

ine pipes and the main pipe, and which at the same time shows how stop-cocks can be dispensed with for such purposes. There is a Y-shaped lead-pipe *a*, whose upper arms are converted into hydraulic lutes by soldering an outer pipe *bb* on to them. The ends of the gas-pipes, both that leading from the stills *c*, and that leading to the gas-main *d*, are widened out into cups dipping into the water which fills the annular space at *b*. When the bell (fig. 2) is raised, the gas-pipe *c* will rise out of the hydraulic lute, and on lowering the bell it will

dip into the lute again. In order to interrupt at will the connection with the gas-main without raising the bell, the indiarubber pipe *c* is raised so that the water contained in it gets up to the junction of the two branches of *a*, and seals them hydraulically.

Stone stills must be made of silicious sandstone or other stone not acted upon by acids and not liable to crack by rapid changes of temperature. Such stone is found at Southowram, and is known as 'Yorkshire flag.' A variety of stone superior to it in resisting changes of temperature is found at Heworth near Newcastle-on-Tyne, but this requires boiling in tar for several days to make it impermeable to acids. In Germany there are also several stones adapted to this purpose, but none equals in excellence the *volvie* lava from the department of Puy-de-Dôme (France). This lava can be had in thick blocks or thin slabs, and requires no boiling in tar to make it acid and heat-proof.

It should be noticed that prolonged submersion in boiling tar is certainly an excellent way of toughening both stones and earthenware (fire-clay), provided they possess a certain degree of porosity. It makes them resist both acids and changes of temperature, and at the same time hardens them very much, so that they must be worked into shape previous to that treatment.

Sometimes chlorine stills and acid tanks are hewn out of a block of stone (especially *volvie*

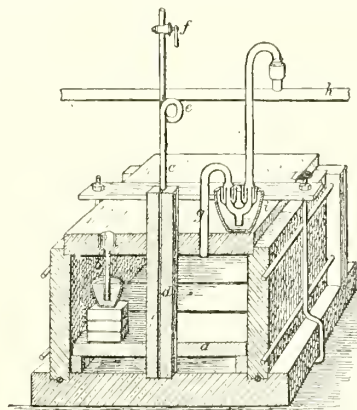


FIG. 4.

lava), but this is a costly operation, and in case a single crack occurs the whole vessel is lost. It is, therefore, more usual (in England probably universal) to build up chlorine stills (like acid tanks, condensers, &c.) from stone slabs joined in a suitable manner and held together by iron binders. Such a still is shown in fig. 4, which represents it cut through in the middle. The bottom is formed by a stone 10 to 12 inches thick, with grooves for the sides to fit in. The sides are stone slabs, 5 to 6, or even 8 inches thick, and joined at the corners either 'on the bevel,' or on the 'feather and groove' principle. In the former case the stones are all dressed in the same way, and are held together by cast-iron corner pieces, drawn together by long screw bolts;

in the latter case the end stones must project both ways over the sides, the latter fitting into grooves of the end stones (as is shown in the figure). The lid consists of one or more stones laid in a rebate. The joints are made tight by dressing a small groove into the two adjoining faces, and either placing a  $\frac{5}{8}$ -inch indiarubber cord in the channel thus formed, or else filling it with an acid-resisting cement. Such cement may be 'black stuff,' that is, coal-tar and fire-clay, kneaded or ground together to the consistency of thick putty, and moulded into balls which are pushed into the joints and stemmed with an iron rod. This cement gets as hard as the stone itself, and stands the hot acid very well. The stones are in any case bedded in such black stuff, and some more of it is stemmed into all joints. Sometimes the joints are made tight by running into them a mixture of melted brimstone and sand or ground clay. Temporary joints, not intended to harden, can be made with a putty of linseed oil and pipe-clay.

The diagram shows how the still is fitted with the following parts. A false bottom *a*; a pipe *b*, for the introduction of hydrochloric acid, sealed at the bottom by the acid itself; a leaden steam-pipe *c*, connected at the bottom with a stone or stoneware steam column *d*, and at the top by the loop *e* with a tap *f* (the loop protecting the tap to some extent against the action of the chlorine); the earthenware or leaden gaspipe *g*, whose connection with the gas main *h* can be opened or shut off at will by putting more or less water into the pot *i*. The man-hole for charging the still and the discharging-hole must be assumed to be provided in that half of the still not shown in the diagram.

These stills are made from 7 × 5 × 3 feet, inside measurement, and upwards.

Fig. 5 shows a still of the bevel-joint type,

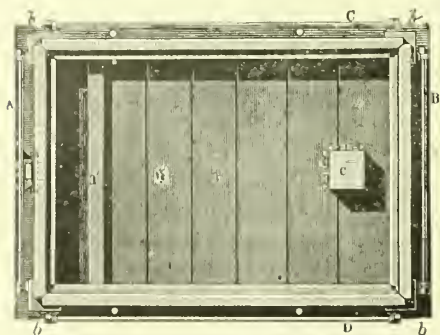


FIG. 5.

seen from above, with the cover removed. *a*, *a* are the flags forming the false bottom, one of which, *a'*, is made to stand up, *c* is the steam-stone, *a* *b* *c* *d* are the rods binding the stones together by means of the cast-iron corner pieces *b*, *b*.

In order to work the stills, those of smaller sizes, where the manganese is contained in a sieve, are usually first charged with the requisite quantity of acid. The sieve containing the manganese (about 1 cwt.) is then put in, the cover is at once put on and made tight by water-luting or cementing, and the evolution of chlorine begins

forthwith. When it slackens, heat is gradually supplied by turning on the steam till the acid is exhausted. The stills are then allowed to cool down, usually till the next morning. They are then opened, the sieve is lifted out, the manganese remaining in it is washed and replenished by more ore, the liquor is siphoned or run out of the still, fresh acid is run in and a new start can be made at once.

The large stone stills are cleaned out after every operation, and are then charged with from 6 to 10 cwt. of manganese, broken up into pieces, which must be smaller in the case of hard ores, but should not be too small, lest too much is washed down below the false bottom. The still is then closed and acid is run in, at first quickly, afterwards gradually, so that it takes several hours to run in the full charge. All this time chlorine is given off, much heat being generated in the process, of course much more with concentrated than with somewhat dilute acid. When the evolution of gas becomes slow, steam is injected into the still, but very cautiously, as otherwise the water might be thrown out of the lutes, and only at intervals, for instance for ten minutes every hour. Too much steaming causes too rapid an evolution of chlorine, and the volatilisation of much acid and water. The temperature of the stills ought never to get above 90 °C. It is preferable not to steam all the stills of a set at the same time, but in regular rotation, to produce a more continuous current of chlorine. Steam of moderately high pressure (40 to 50 lbs. to the square inch) is preferable to weaker steam, because it causes less condensation of water.

Chlorine stills ought to be kept going at least twenty-four hours, but large stills are better kept going for forty-eight hours, which will utilise more of the acid. Even then the liquid, when let out, emits an intolerable stench of chlorine so that this operation is one of the most irksome, both for the workmen and those people who live near the works. Moreover, the 'still' liquor, even after being freed from its muddy constituents by settling, is one of the worst nuisances for any watercourse into which it may be run. In alkali works all this nuisance has been completely overcome by the introduction of the Weldon process, where the still liquor from the fresh manganese ore is run into the Weldon stills, instead of into the drains. At other works where chlorine is made on too small a scale to permit of applying the Weldon or other modern processes, the still liquor ought to be collected in a closed tank, and neutralised by chalk before running it away, even in a very diluted form.

The chlorine evolved in the stills is always contaminated with hydrochloric acid and water. For most purposes these must be removed as far as possible, which is done by conveying the gas in a long string of earthenware or lead pipes, externally cooled by air (or, if needful, by water), so that the water along with the acid condenses into a liquid. This will be greatly promoted by passing the gas through a small column charged with lumps of manganese, where some more chlorine will be given off. Where there is very much acid in the chlorine, as is the case in the Deacon process and in all recent processes for utilising magnesium chloride &c., the acid is first removed by washing the gas with

water in an ordinary acid condenser, and the moist gas can then be dried, if needful, by passing it through a leaden coke-tower charged with sulphuric acid of 150° Twaddell.

The first reaction taking place in the chlorine stills is:  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O}$  or (more probably)  $2\text{MnO}_2 + 8\text{HCl} = \text{Mn}_2\text{Cl}_6 + 4\text{H}_2\text{O} + 2\text{Cl}$ . (There is some discrepancy of opinion as to which of these two chlorides of manganese is formed. Compare W. W. Fisher, C. N. 37, 250; U. S. Pickering, *ibid.* 39, 225; Berthelot, C. R. 91, 251).

These chlorides,  $\text{MnCl}_2$  or  $\text{Mn}_2\text{Cl}_6$ , form a dark-brown solution which quickly decomposes even at the ordinary temperature into  $\text{MnCl}_2$  and free chlorine, so that the ultimate result is:  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + 2\text{Cl}$ ; but this reaction is only completed at about 100°C., and with a certain excess of hydrochloric acid. Theoretically for 100  $\text{MnO}_2$ , or an equivalent quantity of manganese ore, almost exactly 170 dry  $\text{HCl} = 530$  acid of 32° Tw. ought to be consumed; practically, at least 10 p.c. more is used, and with low strength acid, hard manganese, direct steaming, &c., twice the theoretical quantity of acid may be consumed.

*Still-liquor and the processes carried out for utilising it.*—The waste liquor run from the stills contains chiefly manganous chloride, ferric chloride, the chlorides of other metals present in the ore, free hydrochloric acid, and a little chlorine. P. W. Hofmann gives the following analysis of a still liquor, probably from outwardly heated stills:

$\text{MnCl}_2$	•	•	•	•	•	22.00
$\text{Fe}_2\text{Cl}_6$	•	•	•	•	•	5.50
$\text{BaCl}_2$	•	•	•	•	•	1.06
$\text{HCl}$	•	•	•	•	•	6.80
Free $\text{Cl}$	•	•	•	•	•	0.09
$\text{H}_2\text{O}$	•	•	•	•	•	64.55

Black's analysis of still-liquor from ordinary stone-stills, in a well-conducted works, shows how incompletely the acid is utilised there:

$\text{HCl}$	=	6.6220	=	6.622	p.c. $\text{HCl}$
$\text{Al}_2\text{Cl}_3$	=	0.6200	=	0.506	" "
$\text{MnCl}_2$	=	10.5700	=	6.120	" "
$\text{Fe}_2\text{Cl}_6$	=	0.4551	=	0.310	" "
$\text{H}_2\text{O}$	=	81.7329			

13.552

Even if all the Mn had been originally present as  $\text{MnO}_2$ , only an equal quantity of  $\text{HCl}$  to that found as  $\text{MnCl}_2$  (6.12) had escaped as chlorine, so that there was originally

$$13.552 + 6.12 = 19.672 \text{ HCl}$$

present. Accordingly the  $\text{HCl}$  usefully employed was only 62.2, that combined with Fe and Al 4.1, that found uncombined 33.6 p.c. of the whole.

The free acid is tested for in daily practice by a very simple plan. To a measured volume of still-liquor, standardised caustic soda liquor is run in from a burette till the formation of flakes of  $\text{Fe}_2(\text{OH})_6$ , which do not dissolve on shaking, indicate the saturation of the free acid.

Owing to the great nuisance caused by running the still-liquor into ordinary drains or into the local watercourses, where it destroys all fish, damages the masonry, &c., very many proposals have been made for utilising it, partly only with a view to employing the free acid, partly for making the manganese available for other pur-

poses, and partly for regenerating  $\text{MnO}_2$  from them (compare Lunge's Sulphuric Acid and Alkali, 3, 189-197).

Since all these proposals have become obsolete by the development of the Weldon process, we shall here only mention the Dunlop process, which was patented in 1855, and has been practised at St. Rollox for thirty years or more with great success. It consists in removing the free  $\text{HCl}$  and  $\text{Fe}_2\text{Cl}_6$  by agitating the liquor with ground chalk (exactly as in the Weldon process), pumping the neutral solution of  $\text{MnCl}_2$  and  $\text{CaCl}_2$  into large horizontal cylinders fitted with agitating gear, mixing it with the quantity of ground chalk required for converting the  $\text{MnCl}_2$  into  $\text{MnCO}_3$ , and producing this conversion by agitating under a steam pressure of 2-2½ atmospheres. The precipitate of  $\text{MnCO}_3$  is settled out, washed, pressed, partially dried, and then oxidised by being exposed to a current of air in an oven heated to about 300°C., which is always kept moist. In 24 hours the process is complete. The paste is now found to consist of 72 p.c.  $\text{MnO}_2$ , 26 p.c.  $\text{MnO}$ , and 2 p.c.  $\text{CaCO}_3$ . This process is only remunerative where fuel is cheap, and as it requires very costly plant it has never spread beyond the place of its origin, where it has also at last had to give way to the Weldon process, and is now only employed for the production of an artificial oxide of manganese for glassmaking.

*The Weldon process for making chlorine.*—

The process bearing the above name has, like most other important inventions, been perfected by many successive improvements. Many of its features had been foreshadowed by former inventors; but without the indomitable energy of the late Walter Weldon, and the efficient practical help rendered to him at Messrs. Gamble & Co.'s works at St. Helen's, it would have remained futile like all its predecessors. Weldon's first attempts were made in 1866; in 1869 chlorine was first actually manufactured by Weldon mud. By carefully studying all the conditions of the reaction on the large scale, at last all obstacles were overcome and the fullest practical success was secured. This achievement alone entitles Mr. Weldon to be called one of the greatest benefactors to chemical industry.

The leading idea of the Weldon process is the following. We start with a solution of manganous chloride—*i.e.* ordinary still-liquor. This is deprived of free acid and ferric chloride by agitation with calcium carbonate under ordinary atmospheric pressure. To the neutral settled solution of  $\text{MnCl}_2$  and  $\text{CaCl}_2$  is added milk of lime more than sufficient for precipitating all manganese as  $\text{Mn}(\text{OH})_2$ , so as to leave about half as much lime in excess, both lime and manganous hydrate being partly suspended and partly dissolved in a solution of  $\text{CaCl}_2$ . This pasty mixture is treated with a strong current of air, at a slightly raised temperature, when the oxygen acts upon it, forming principally a compound of  $\text{MnO}_2$  and  $\text{CaO}$ . By adding a further quantity of  $\text{MnCl}_2$  and blowing in more air the quantity of  $\text{CaO}$  is reduced, the ultimate limit in ordinary cases being a compound of  $\text{1CaO}$  with  $2\text{MnO}_2$ ; sometimes, however, mud containing less than 0.5 base has been obtained. The oxidation is now stopped; the thin paste or



mud is run into tanks, where it separates into a thicker mud and a supernatant clear solution of  $\text{CaCl}_2$ . The latter is run to waste, the former, now called 'recovered manganese' or 'Weldon mud,' is still liquid enough to be run into a special kind of still, where it is decomposed by hydrochloric acid, yielding chlorine gas and a mixed solution of  $\text{CaCl}_2$ ,  $\text{MnCl}_2$ , and a little uncombined  $\text{HCl}$  (much less than in the old process of working with native ore). This solution serves again as the starting-point for the recovery of  $\text{MnO}_2$  in the way just described.

It will be seen that in this process it is the atmospheric oxygen supplied by the blowing engine which effects the liberation of  $\text{Cl}$  from  $\text{HCl}$ . The manganese compounds serve merely as carriers of oxygen, exactly as the nitrogen oxides in the manufacture of sulphuric acid, and are used over and over again, but a small loss of these oxygen carriers cannot be entirely avoided in practice.

Long before Weldon's patents existed it had been, of course, known that precipitated manganese protoxide could be more highly oxidised by means of atmospheric air. But Weldon was the first to find out that oxidation of  $\text{MnO}$  to  $\text{MnO}_2$ —a compound of distinctly acid properties—can only take place in the presence of a base which combines with it at the moment of its formation. If the only base present be  $\text{Mn}(\text{OH})_2$ , then the  $\text{MnO}_2$  will combine with it to form either  $\text{MnO}, \text{MnO}_2$ , or else  $2\text{MnO}, \text{MnO}_2$ , according to the temperature. Thus, when  $\text{MnO}$  is the only protoxide present, one half of it at most can be oxidised into  $\text{MnO}_2$ , the other half being required to furnish the necessary base for combining with  $\text{MnO}_2$ . If, however, another soluble protoxide be present, the  $\text{MnO}_2$  combines with this instead of with  $\text{MnO}$ . The only other protoxide practically available is lime, which is sufficiently soluble in a solution of calcium chloride. If instead of  $\text{MnO}, \text{MnO}_2$ , we produce  $\text{CaO}, \text{MnO}_2$ , there is, of course, no advantage gained with respect to the consumption of acid, since in either case  $6\text{HCl}$  are required to liberate  $2\text{Cl}$ . But the advantage lies in this, that the absorption of oxygen by  $\text{Mn}(\text{OH})_2$  in the presence of dissolved lime is enormously more rapid than in the absence of a soluble base. The product of oxidation of  $\text{Mn}(\text{OH})_2$  by itself would be much more costly than native manganese.

It is not possible to employ a full equivalent of lime to each of  $\text{Mn}(\text{OH})_2$ , so as to form  $\text{CaMnO}_3$ , because there cannot be present sufficient  $\text{CaCl}_2$  to hold it in solution. Hence only enough  $\text{Ca}(\text{OH})_2$  is used to convert 0.6 of the  $\text{Mn}$  into calcium manganite, the other 0.4 of the manganese present is converted into manganite of manganese,  $\text{MnMnO}_3$ .

When thus 60 equivalents  $\text{CaMnO}_3$  and 40  $\text{MnMnO}_3$  have been formed, a further quantity of neutral solution of  $\text{CaCl}_2$  and  $\text{MnCl}_2$  ('final liquor') is mixed with it, and the injection of air is continued. At the temperature employed  $\text{MnCl}_2$  can act upon half of the lime of  $\text{CaMnO}_3$ , forming a compound of one  $\text{CaO}$  with two  $\text{MnO}_2$  and  $\text{Mn}(\text{OH})_2$ , which is at the same time oxidised to  $\text{Mn}_2\text{O}_3$  or  $\text{Mn}_2\text{O}_4$ . The final product is a thin black mud, consisting of a solution of  $\text{CaCl}_2$  holding in suspension a mixture of man-

ganites of manganese with an acid manganite of calcium.

The following is the description of a Weldon plant, according to recent designs. On the diagram fig. 6,  $\text{DD}$  are the mud-stills, of which there should be three or four, and which will be described in detail hereafter. There is, besides, an ordinary still  $\text{E}$ , which serves for dissolving native manganese ore, to make up for the loss in recovery, and which is so fixed that its waste liquor can be discharged directly into one of the mud-stills.  $\text{GG}$  are the neutralising wells into which the manganese liquor from  $\text{DD}$  is discharged, and where it is mixed with ground chalk or limestone dust by means of the agitator  $\text{F}$ , in order to remove the free  $\text{HCl}$  and the iron.  $\text{H}$  is a cast-iron pump with gun-metal piston, valves, &c., which forces the neutralised liquor into the chloride of manganese settlers  $\text{AA}$ . The suction pipe which dips in the acid liquor is very quickly corroded unless it is made to turn on a swivel so as to lift it out before running acid liquor into the well. The settlers  $\text{AA}$  (of which there must be at least two, or better, more) are made of wrought or cast iron, which is not acted upon by the neutralised liquor. In one of these tanks the muddy liquor is allowed to settle while the other one is being filled. They are provided with cocks or valves, continued inside into swivel pipes or indiarubber tubing, by which the liquor can be run off from any part of the tank without disturbing the sediment. The discharge pipes unite outside in an iron pipe, which divides again into two branches, one for each of the two oxidisers  $\text{B}$  (only one of which is shown here), into which they enter at about two-thirds or three-fourths of their height. Each settler also has a large conical bottom valve for removing the mud from time to time, by means of the pipes  $\text{G}$ .

If the settlers  $\text{AA}$  are each  $18 \times 12 \times 6$  feet, they hold, when full, about 50 tons, and then weigh altogether upwards of 100 tons. They must, therefore, be very firmly mounted on a strong timber framework of 12 or 14-inch beams, resting on the same foundation as the manganese mud settlers.

The oxidisers  $\text{B}$  in which the recovery proper takes place are wrought-iron cylinders open at the top, with a flat bottom, fixed at such a height that there is sufficient fall for the manganese mud into the settlers  $\text{CC}$ , and from these again into the stills  $\text{D}$ . They are charged with settled  $\text{MnCl}_2$  liquor from  $\text{AA}$  to about two-thirds of their height, and with milk of lime either directly from the tank  $\text{J}$  by the pump  $\text{K}$ , or, preferably, from a tank fixed above the oxidisers and fitted with separate regulating valves for each oxidiser. This tank (not shown here) should be provided with a branch of the air-pipe or with a separate injector for stirring up its contents. The 7-inch pipe  $\text{L}$  conveys compressed air (furnished by the blowing engines  $\text{I}$  and the air-vessel  $\text{M}$ ) into the oxidisers; it is carried over the top of  $\text{B}$  down to the bottom, and there branches out into a cross of pipes  $\text{N}$ , perforated with a number of holders for dividing the current of air. Each oxidiser also has a 2-inch steam pipe (not shown here) which equally passes over the top down to the bottom and there branches out into a perforated cross.

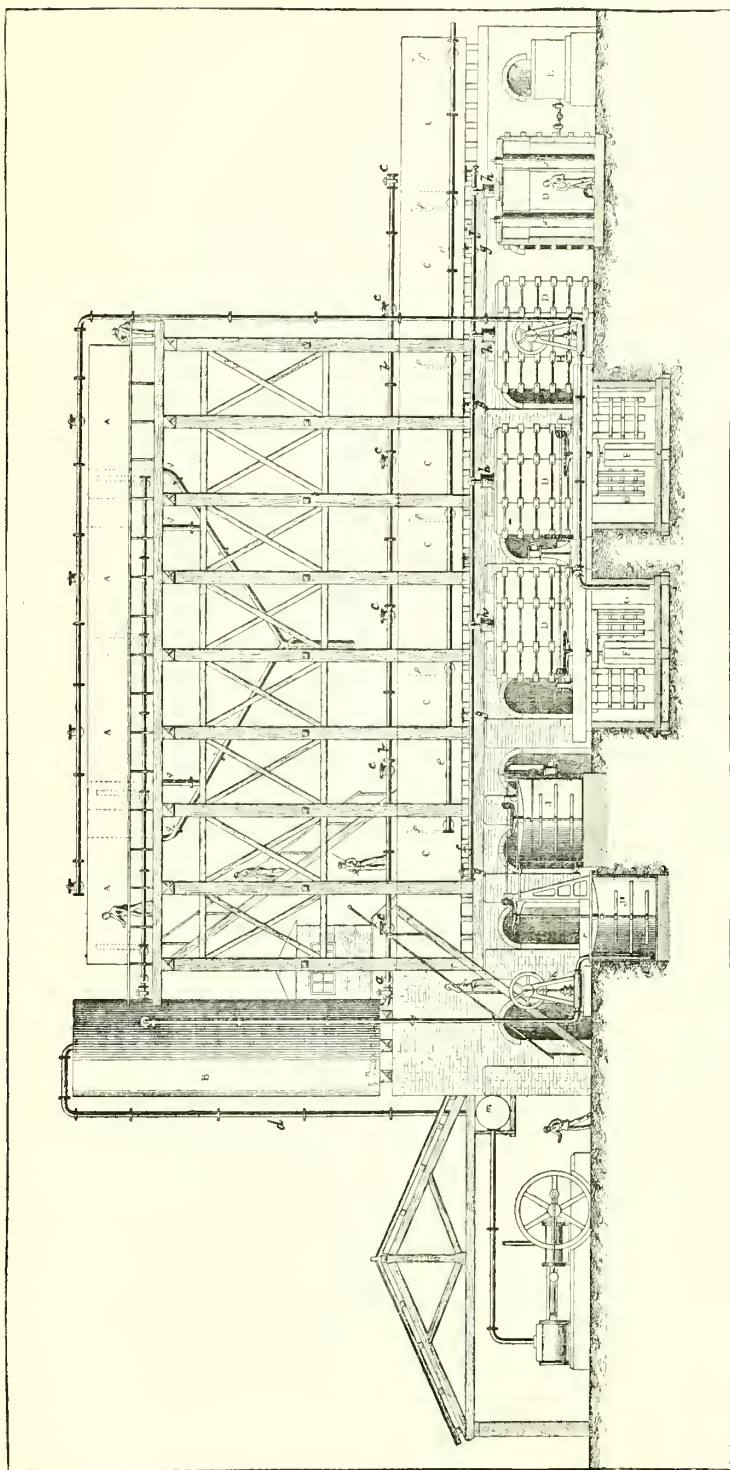


Fig. 6.

None of the pipes are directly connected with the shell of  $n$ , as the shaking during the blowing would loosen the joints; the only fixed connection which cannot be dispensed with, that with the  $MnCl_2$  liquor pipe from  $aa$ , should be made yielding by interposing an india-rubber pipe of equal width (1 inch). Lastly, there are discharge valves  $a$ , connected with a common pipe  $b$ , which sends out a branch with 4-inch valves  $cc$  over each mud-settler  $cc$ . These mud-settlers, of which there must be at least four, better six, are fitted with 2-inch swivel-pipes  $p$  for running off the  $CaCl_2$  liquor, communicating with a pipe or shoot  $e$ , leading to a catch-well, and at the bottom with a 4-inch pipe  $f$  with sluice-valves  $gg$ ; from which each of the stills  $dd$  is fed by a pipe and sluice-valve  $h$ .

The engine is here shown as a horizontal twin-engine. Others prefer vertical blowing engines, and generally the larger they are made the better. For each ton of bleaching-powder to be made, about 300,000 cubic feet of air, or one hour's work of 40 to 45 horse-power, may be taken as necessary. The exhaust steam should be utilised for heating up the feed, the milk of lime, &c.

(This figure is taken from one of Mr. Weldon's publications, where it is stated as the *ordinary* rate of supply, whilst in special cases much less than that, down to 158,000 cubic feet of air, were required. The figure of 300,000 cubic feet would certainly prove an extremely incomplete absorption of the oxygen (less than 5 p. c. of that injected), and it would require much more than 45 horse-power per hour.)

The milk of lime is made in the two iron cylinders  $j$  and  $j'$ , each about 6 feet high and 7 or 8 feet wide;  $j$  serves for slaking the lime and preparing the milk,  $j'$  for storing it and supplying it to the lime-pump  $k$ . A donkey-engine bolted to  $j$  drives the agitators of both cylinders.  $j$  has a perforated cage in which the quicklime is put in order to be slaked by the water contained in the cylinder.

The neutralising wells  $gg$  are sunk in the ground, and are surrounded by a clay puddle. They are made of large stone slabs in an octagonal shape, or of freestones in a circular shape, always of course so as to be altogether acid-proof. It is most important that there should be no loss of liquor from this well.

The chlorine stills belonging to this plant (Weldon stills or mud stills) are very much larger, especially much higher, than the ordinary manganese-ore stills. The shape usual at small works is of square section about 7 feet  $\times$  7 feet, and 8 or 9 feet high. For large works they are made octagonal (as shown in fig. 6, and more in detail in figs. 7 and 8), sometimes 12 feet wide and high. The bottom is made in two pieces, held together by corner brackets and bolts  $aa$ . The sides, also in two tiers, are joined in the corners by india-rubber cords or bands; they are bound together by the brackets  $bb$  and screw bolts, or by cable chains, drawn up tight by coupling screws, and pressing on wooden posts outside of the still-sides. The cover is usually made dome-shaped. We note the funnel for manganese mud,  $d$ , the steam-stone  $c$  resting in the socket  $p$ , the discharge-cock  $f$ , the gas-pipe  $l$ , the acid-supply pipe  $e$ , about half-way up

the height of the still. There must be also a man-hole, a stoneware cock with a glass tube for a liquor gauge, and a small testing-cock, all of them not shown in the diagram.

We shall now describe the round of operations, beginning with the running of spent liquor

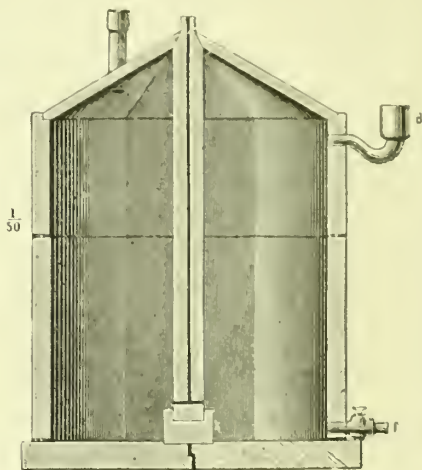


Fig. 7.

from the mud stills into the neutralising well. The latter should be covered over, a pipe leading the gases (never free from chlorine) into a high chimney—if necessary, through a milk of lime tower. The liquor is here neutralised with ground chalk or limestone dust, of which no

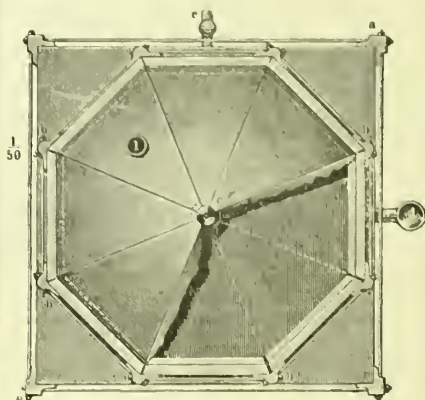


Fig. 8.

more than is absolutely necessary should be employed. This is best effected by grinding the calcium carbonate with water (or preferably with still-liquor itself) into a milk, and running this in, with constant agitation, till no more  $CO_2$  is given off and till there is no more acid reaction upon litmus paper. This operation will remove the free  $HCl$  and the  $Fe_2Cl_6$ , causing a precipitate of  $Fe(OH)_3$ , but  $MnCl_2$  is not acted upon here. (Further on we shall mention the proposal of G. E. Davis for neutralising the still-liquor, pre-



viciously freed from sulphate of lime by subsidence, by fresh manganese mud, whose base would thus be removed to a great extent.)

The neutralised liquor, along with all the mud, is now pumped into the liquor-settlers at the top of the timber staging, where it must be completely clarified before being run into the oxidisers. Any matter remaining in suspension greatly interferes with the recovery process, and especially causes very troublesome frothing in blowing. The muddy deposit remaining in the settlers is run off from time to time through the bottom valve. This deposit formerly caused the principal loss of manganese in the Weldon process, by mechanically keeping a quantity of  $\text{MnCl}_2$  in suspension and wasting it. But this can be avoided by removing the  $\text{MnCl}_2$  from that deposit as much as possible, either by systematic washing or by a filter-press, and reintroducing this  $\text{MnCl}_2$  into the process. It is, of course, desirable to keep the bulk of the deposit as small as possible by not employing more calcium carbonate than is really necessary, and by employing hydrochloric acid containing very little sulphuric acid, which by the formation of  $\text{CaSO}_4$ , very much increases the bulk of the insoluble matters. We have seen above that the hydrochloric acid is sometimes specially purified for this purpose by means of  $\text{CaCl}_2$  or  $\text{BaCl}_2$ . Principally by attending to a thorough exhaustion of this settler-mud—of course, together with carefully attending to all other manufacturing details—the consumption of fresh manganese ore, which at first often amounted to 10 p.c. of the weight of bleaching powder made, has in the best works been brought down to 1 p.c.

The washed mud, which contains  $\text{Fe}_2(\text{OH})_6$ , and a little  $\text{MnCl}_2$ , may be employed for purifying coal-gas from  $\text{H}_2\text{S}$ . It has been employed by G. Lunge for deodorising the drainage from old soda-waste heaps; by spreading out the resulting mass, containing  $\text{FeS}$  and  $\text{MnS}$ , in contact with air, it may be revived and used over again.

The clarified liquor drawn off from this deposit is essentially a solution of  $\text{MnCl}_2$  and  $\text{CaCl}_2$ . The latter is not merely an accidental admixture, but it is absolutely necessary to the success of the process that the proportion of  $\text{CaCl}_2$  to  $\text{MnCl}_2$  should not fall below  $\frac{1}{2}$  to 1. This seems to be owing to the circumstance that a solution of  $\text{CaCl}_2$  keeps much more  $\text{Ca}(\text{OH})_2$  in solution than water, in the shape of an oxychloride, and that this is necessary to expedite the subsequent reactions. Normal  $\text{MnCl}_2$  liquor contains enough  $\text{MnCl}_2$  to form about  $3\frac{1}{2}$  lbs.  $\text{MnO}_2$  per cubic foot.

The liquor is run into one of the oxidisers till this is rather more than half full; the other half serves for containing the milk of lime, the 'final' liquor,' and, above all, the froth formed during the operation.

While one of the oxidisers is being charged and heated up, the other one is under blast, so that the operation is a continuous one. The liquor must be heated up to  $55^\circ\text{C}$ . by blowing in steam, but, when continuously working, it often has that temperature to begin with, at least in summer, owing to being heated in the stills.

The next operation is adding milk of lime. The lime employed for the Weldon process ought to be as pure as possible, and ought

especially not to contain more than 1 p.c. of magnesia. It ought to be particularly well burnt and slaked, and completely separated from unburnt or unslaked (dead) particles by being strained through a fine wire. Those particles cannot aid in the recovery of  $\text{MnO}_2$ , and they remain in this as injurious 'base.' The slaking takes place by directly introducing the quicklime into hot water, throwing it into the cage within the vessel J (fig. 6), and agitating all the time. The coarser impurities remain behind in the cage, the finer ones in a drainer interposed between J and J'. The finished milk of lime in J' contains from 20 to  $22\frac{1}{2}$  lbs. of  $\text{CaO}$  per cubic foot, and is pumped into the top cistern, from which it can be let down in a preferably regular stream, provided that it is kept agitated in that cistern itself (*cf. supra*).

In order to begin an operation, one of the oxidisers is half-filled with well settled  $\text{MnCl}_2$  liquor (of which a stock must be in reserve for 'final liquor'), and is heated up to  $55^\circ$ . The blast is put on slowly, and milk of lime, of which the initial level in the store tank has been carefully noted, is run in till all manganese has been precipitated as  $\text{Mn}(\text{OH})_2$ . This point is ascertained by frequent testings, both by trying whether red litmus paper turns blue (from an excess of lime), and by filtering a small sample and ascertaining by the addition of strong bleach liquor whether the filtrate turns brown in consequence of containing some  $\text{MnCl}_2$ . When this reaction ceases, the flow of lime is at once stopped, and the quantity consumed so far is read off on a gauge. This is merely done to be able to fix upon the further quantity of lime, which ought to be from one-third to one-fifth of that first used. The exact quantity of excess lime to be used must be ascertained at each works by independent trials, as it varies according to the nature of the raw materials, &c.

The 'excess-lime' is run in immediately after the first, and the blast is now at once put on with full strength; otherwise a 'thick batch' would be produced, whilst a 'red batch' (containing  $\text{Mn}_2\text{O}_3$ ) is formed when the blast is put on too soon. The oxygen contained in the blast now acts upon the mixture of manganous and calcium hydrates, and forms a manganite of calcium,  $\text{CaMnO}_3$ , along with manganite of manganese,  $\text{Mn}_2\text{O}_3$ .

This means that at this stage each molecule of  $\text{MnO}_2$  is combined with a full molecule of 'base,' either  $\text{CaO}$  or  $\text{MnO}$ ; but this amount of base must be reduced because otherwise too much acid is consumed, all the more as the base is swelled by  $\text{MnO}$ ,  $\text{CaCO}_3$ , and  $\text{Fe}_2\text{O}_3$  present as impurities, since first of all the base must be saturated before the  $\text{MnO}_2$  can be acted upon. Although there is no theoretical impossibility against it, there seems to be no practical way of getting the base below 0.5, or even quite down to that point; 0.6 is considered very good, and 0.7 is the more usual amount. Sometimes batches have been found to contain only 0.5 p.c. base, of course including the impurities. In many cases this may be owing to the testing methods employed, which do not permit any very high degree of accuracy, and, as carried out in the works' laboratories, might easily cause an error amounting to 0.1 base or more. But it cannot be denied

that such a low base has also been noticed by observers of indubitable competency, so that it must be assumed that, exceptionally, calcium manganites can be formed of a more acid type than  $\text{CaO}, 2\text{MnO}_2$ .

With 0.7 of base, the Weldon mud consumes 5.4 HCl for each 6 HCl that would be required for  $\text{Mn}_2\text{O}_3$ ; pure  $\text{MnO}_2$  would only require 4 HCl, but native manganese ore practically requires much more acid than Weldon mud, in spite of the base of the latter, since it is so much more difficult to dissolve.

It is, however, not possible to arrive at a proper result by the simple blowing of air into the mud of calcium and manganous hydrates. With 0.6 equivalent of excess of lime, the degree of oxidation obtained is usually about 86 p.c., the product before the addition of 'final liquor' consisting of 0.14 equivalents of  $\text{MnO}_2$  combined with 0.14  $\text{MnO}$ , 0.48  $\text{MnO}_2$  with 0.48 CaO as  $\text{CaMnO}_3$ , and 0.24  $\text{MnO}_2$  with 0.12 CaO as  $\text{CaMn}_2\text{O}_7$ . There is thus 0.74 total protoxides to 0.86  $\text{MnO}_2$ , or 0.86 equivalents of base per 1 equivalent of  $\text{MnO}_2$ . In order to reduce the base, some more chloride of manganese liquor is run in ('final liquor'), up to the point that a filtered sample gives the reaction upon  $\text{MnCl}_2$ . In this case 0.24 eq. of  $\text{MnCl}_2$  will have been used, taking away half of the lime in the 0.48 eq.  $\text{CaMnO}_3$ . If the blowing in of air is now continued until the absorption of oxygen ceases, the 0.24 eq. of  $\text{MnCl}_2$  added will have been converted into  $\text{Mn}_2\text{O}_3$  or  $\text{Mn}_3\text{O}_4$ , according to temperature. In the former case the base will be reduced from 0.86 to 0.7, but at the same time the average degree of oxidation from 86 to 75.8 p.c.; in the latter case the base will be 0.632, the degree of oxidation 79 p.c.

It should be noticed that these calculations only refer to the combined base, but do not include  $\text{MgO}$ ,  $\text{CaCO}_3$ ,  $\text{Fe}_2\text{O}_3$ , &c. which must be included in the ordinary method of testing for total base. With good work the total base does not exceed 0.7.

In actual practice it is not possible to add the lime exactly as indicated by theory, for when the bleaching powder reaction in the filtered sample has ceased, decidedly more than 1 eq. of CaO has been added to 1 of  $\text{MnCl}_2$ ,  $\text{Mn}(\text{OH})_2$  being soluble to a certain extent in  $\text{CaCl}_2$ ; nor do all the molecules of lime instantly act upon  $\text{MnCl}_2$ , but they will do so afterwards. Actually from 1.1 up to 1.45 eq. of CaO is used at first, and this is brought up to 1.6 by the 'excess lime.' With that quantity a well-settling mud is obtained, from which a good deal of  $\text{CaCl}_2$  solution can be drawn off, thus obtaining stronger manganese mud for the stills. Usually 12-14 cwt. of lime per ton of bleaching powder are required for the recovery process (i.e. about as much as in the bleaching powder chambers).

The operation of blowing is carried out in this way. Tests are taken from time to time; it is ascertained whether the alkaline reaction continues, which ought to be the case perceptibly for at least an hour after the commencement of the blowing; also, whether the oxidation proceeds any further or not. When the latter is the case, some more  $\text{MnCl}_2$  liquor is run in, without stopping the blast, until a filtered sample yields the brown reaction with bleach liquor. After a

few minutes this reaction ceases, all dissolved  $\text{MnCl}_2$  having been precipitated. Then a little more final liquor is added, and the blowing is continued, and this is repeated till it takes a somewhat long time to 'blow out' the manganese. This must be certainly performed before running the batch into one of the settlers.

It has been found decidedly preferable to apply a very strong current of air by means of a powerful blowing engine; in this way the work is not merely done in much less time, but with a smaller absolute amount of air than with smaller engines. The time should not exceed 2½ hours, nor the quantity of air 300,000 cubic feet per ton of  $\text{MnO}_2$ . With very deep oxidisers even better results can be obtained.

The manganese mud, as it runs from the oxidisers, must be concentrated before entering the chlorine stills, since it would otherwise become indefinitely diluted by the acid, the milk of lime, &c. This is done by allowing it to remain some time in the mud-settlers at the base of the oxidisers, where in a few hours it separates into a thicker mud and a clear solution of  $\text{CaCl}_2$ . The latter is run off by means of a swivel-pipe, and before running into the waste drain it is made to pass through a catch-well, where any  $\text{MnO}_2$  carried away may be saved. The thicker manganese mud remaining behind, containing up to 17 lbs.  $\text{MnO}_2$  per cubic foot, is still liquid enough to be run in pipes and through sluice-valves into the chlorine stills.

The working up of the manganese mud takes place in this way. First, a charge of hydrochloric acid is run into the still, say 2 feet deep; in lieu of part of this, still-liquor from native manganese ores may be employed. Then manganese mud is run in slowly by means of a sluice-valve. Since in this fine state of division the action between  $\text{MnO}_2$  and HCl is practically instantaneous, a perfectly uniform current of chlorine can be obtained by regulating the flow of manganese mud. When the liquid taken out at the test-cocks begins to assume a dark colour, a little steam is blown in. The end is reached when the liquor, in spite of a sufficient temperature, is clear but coffee-coloured, and on pouring upon chalk produces only a slight effervescence. It ought not to contain more than 0.5 p.c. free HCl if tested like ordinary still-liquor (*cf. supra*). If the saturation of the HCl is driven too far, there is danger of some  $\text{MnO}_2$  remaining behind, and getting lost with the mud from the  $\text{MnCl}_2$  settlers. Each operation in the stills lasts from 4 to 6 hours; the liquor is then run into the neutralising well, and the round of operations begins anew.

The yield of chlorine by the Weldon process is mostly expressed in terms of the quantity of the salt required to be decomposed for manufacturing 1 ton of 37 p.c. bleaching powder. This depends to some little extent on the management of the Weldon process itself, good saturation and thick mud consuming less HCl than *vice versa*, but much more upon the previous operation of condensing the HCl in the salt-cake process. Where open roasters are employed and only the pot-acid is used, 1 ton of bleach generally requires from 70 to 80 cwt. of salt, although sometimes 63 cwt. are found sufficient. With close roasters, where the

roaster acid is used as well, and with a very well managed process, 1 ton of bleach can be made from about 50 cwt. of salt, or even a little less, but the average is 60 cwt. of salt (Weldon, S. C. I. 1883, 108).

If the yield is calculated from the hydrochloric acid itself, from  $3\frac{1}{2}$  to 4 tons of strong acid, or say, 24 cwt. of HCl, is consumed for 1 ton of strong bleach. Since the chlorine contained in the latter only amounts to  $7\frac{1}{2}$  cwt., the Weldon process utilises little more than 30 p.c. of the HCl, the remainder going to waste in the shape of  $\text{CaCl}_2$ .

The consumption of coal, not including the burning of limestone, amounts to 16 cwt. per ton of bleach, on an average of all works, some requiring considerably less; that of lime is about 13 to 14 cwt. for the oxidisers and as much for the chambers, and about 5 cwt. of limestone or chalk-dust for neutralising. The cost of labour is hardly greater than when using native ore without any recovery.

The total cost of bleaching powder by the Weldon process in 1883 is stated by G. E. Davis as follows (S. C. I. 1883, 155):

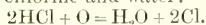
	£	s.	d.
Fuel . . . . .	0	4	6
Lime for oxidiser . . . . .	0	10	8
Lime for powder . . . . .	0	10	8
Limestone dust . . . . .	0	2	2
Manganese . . . . .	0	3	0
Wages . . . . .	0	15	0
Casks . . . . .	0	17	0
	£3	3	0

This does not include interest on capital, management, wear and tear, depreciation, &c., nor is there any value put upon the hydrochloric acid.

#### CHLORINE PROCESSES EMPLOYING ATMOSPHERIC OXYGEN FOR THE LIBERATION OF CHLORINE.

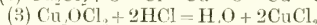
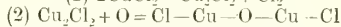
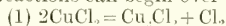
*The Deacon process.*—After many unsuccessful attempts made by Oxland (1840), Jullion (1846), Binks (1860 and 1862), Dufrené (1863), and others, the labours of H. Deacon and F. Hurter, in the years from 1868 on, produced an entirely successful chlorine process which is founded on the direct oxidation of the H in HCl by atmospheric oxygen, and which utilises much more of the HCl than any process employing either native or recovered  $\text{MnO}_2$ . Some processes patented after theirs (Henderson, 1871, Weldon, 1871, Wigg, 1873, &c.) proceed on the same lines, but have not been practically successful.

The Deacon process starts from the well-known fact that a mixture of hydrochloric acid and oxygen at a certain temperature, especially in contact with porous substances, partially changes into chlorine and water:



This decomposition is very much assisted by the employment of substances which serve as oxygen carriers, and of these the salts of copper (previously employed by Vogel 1855, Gatty and Laurent, 1860, Mallet, 1866) have been found most useful. Probably in all cases cupric chloride is formed, which at once splits up into cuprous chloride and free chlorine. The  $\text{Cu}_2\text{Cl}_2$

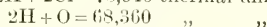
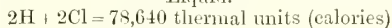
combines with oxygen to form oxychloride,  $\text{CuO.CuCl}_2$ , and this acts again upon HCl, yielding water and reforming cupric chloride, so that the reactions can begin over again:



Theoretically *all* the HCl would thus be converted into chlorine, but in practice under the most favourable circumstances only half of this decomposition is effected. The undecomposed HCl is, however, not lost, but is recovered and can be utilised for other purposes, e.g. for the Weldon process.

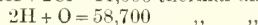
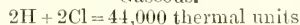
Hurter (S. C. I. 1883, 105 and 107) has studied the thermal conditions of this change. He points out that a direct decomposition of liquid hydrochloric acid by oxygen in the free state is an impossibility, whilst in the gaseous state HCl can be decomposed directly by free oxygen; for:

Liquid.



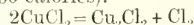
Deficiency 10,280

Gaseous.



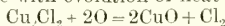
Excess 14,700

But although, as we see, in the gaseous condition the reaction  $2\text{HCl} + \text{O} = \text{H}_2\text{O} + \text{Cl}_2$  evolves heat, it is a slow and very incomplete reaction. The case becomes, however, quite different by bringing in the assistance of copper compounds, of which cupric chloride is most active, owing to its capability of dissociation, that is, of converting heat into chemical energy. At a temperature approaching 400° C. it splits up into cuprous chloride and chlorine, with absorption of heat (37,500 calories).



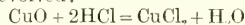
103,260 cal. = 65,760 + 37,500 calories absorbed.

If the cuprous chloride at a high temperature is exposed to a current of oxygen, it forms cupric oxide with evolution of heat:



65,760 cal. = 74,320 - 18,560 calories evolved.

If CuO is changed into  $\text{CuCl}_2$  by HCl, there is also heat evolved:



37,160 + 44,000 = 51,630 + 57,000 - 27,470 evolved.

Thus the total amount of heat evolved during the cycle of reactions is greater than that absorbed during the dissociation of cupric chloride. Once the dissociation has begun, the cycle of reactions must continue as long as HCl and O are present. But, similarly as in other processes of dissociation, the evolution of chlorine ceases immediately when the chlorine exerts a certain pressure (tension). The higher the temperature the greater may be this pressure until a temperature is reached at which  $\text{CuCl}_2$  can no longer exist. At the temperature of its complete dissociation, a current of hydrochloric acid and air will no longer be affected by the presence of copper.

From a diagram constructed by Hurter, showing the affinity of technically available



elements to oxygen, chlorine, and hydrogen, it appears that no other metal than copper forms two oxides and two chlorides, in which the combination is of so loose a character. It is therefore almost a certainty that a cheaper and equally efficient catalyte cannot be found, and that the Deacon process is the best for the direct conversion of gaseous HCl into free chlorine.

Deacon's process deals with the gaseous hydrochloric acid, as it is evolved in decomposing common salt by sulphuric acid, without condensing it into liquid acid. This is evidently a great advantage in one way, but it has the drawback that in the beginning of each operation much more HCl, and hence more Cl, is got than afterwards. This want of uniformity is less felt with the mechanical salt-cake furnaces, *e.g.* Mactear's, which, however, yield the HCl too much diluted with air and inert gases. In practice only the gases from the decomposing pots, say 68-70 p.c. of the total HCl, are used for the Deacon process, those coming from the roasters being too dilute and containing too much sulphuric acid. In order to equalise the operation to a certain extent, two pots can be combined in this way, that only the strong gas escaping in the first stage of the decomposition of NaCl is passed through the Deacon apparatus; when half the time is over, the gases are turned into an ordinary acid condenser, and those from the second pot freshly charged are turned into the Deacon apparatus. It does not appear that this is usually followed.

The quantity of air necessary to form chlorine enters through the joints of the doors and dampers. It is regulated by the speed of the aspirator (a Root's blower) which is placed at the end of the whole apparatus and produces the movement of the gases through it. Usually there are 4 vols. of air to 1 vol. of HCl. An excess of air is less injurious than a deficiency of it, in which case there is an incomplete decomposition, and the acid condenser, which is not calculated for more than the regular quantity of HCl, will easily let some HCl pass through, thus causing double damage.

The gases leaving the pot are first cooled by a long string of pipes and a scrubber; thus much of the water and about  $\frac{1}{5}$  or  $\frac{1}{6}$  of the HCl is removed. A patent by Deacon and Hurter (Pat. 2,101, 1888) provides for cooling the gas and drying it in a sulphuric acid tower before it enters the decomposer, such complete drying being very advantageous for the process. The gases now enter the heating apparatus. This is a furnace, 16 feet  $\times$  16 feet, in which twenty-seven vertical pipes, 12 inches wide and 9 feet high, are arranged in two sets of twelve each, connected like the 'breeches-pipes' in the blast-heating stoves, formerly used in iron works and now replaced by brick heaters.

The gases are here heated up to 500°; the waste heat of the furnace is sufficient for heating the decomposer, which does not possess any fire of its own.

The gases now pass into the decomposer (fig. 9). This is an upright cast-iron cylinder, 12 to 15 feet wide. It contains a cylindrical ring of broken bricks, supported by cast-iron shutters. The gases enter at the circumference at A, pass

radially across the decomposing-mass D into the inner space, and are led away through the pipe C. The annular space between the shutters is 3 feet wide, and is divided into six compartments, one of which is emptied every fortnight. This is done by means of the discharging doors CC below the cylinders. Fresh decomposing-material is then thrown in from above through E; this material consist of burnt clay broken up into lumps, freed from dust, and dipped into a solution of cupric chloride. The mass contains about 0.6-0.7 p.c. of metallic copper. After the active substance has served once, that is, for ten to twelve weeks, it is thrown away. Each cwt. of clay produces about

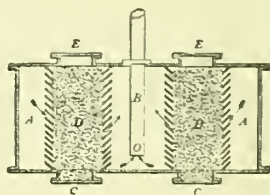


FIG. 9.

10 to 12 cwt. of bleach. It has been found useless to attempt utilising the contact substance by re-dipping it in the copper solution or in any other way. The cost of copper for the contact substance does not exceed 1s. per ton of bleach produced.

The temperature both in the heating apparatus and in the decomposer must be most carefully regulated, for which purpose special pyrometers have been constructed (*cf.* Hurter on Pyrometers, S. C. I. 1886, 625). In the decomposer it ought to range from 180 to 500°C.

When the gases leave the decomposer they consist of a mixture of HCl, free Cl, and steam. In the best case  $\frac{1}{2}$  of the HCl is converted into Cl, but sometimes only  $\frac{1}{5}$ . They are now cooled by passing through a long string of earthenware or glass pipes, and are then freed from HCl by washing with water in the ordinary acid condensers, consisting of stone coke towers, combined or not combined with acid cisterns, Woulfe's jars, &c. By properly managing this process, most or all of the acid can be obtained in the strong state, as required for the Weldon process and other purposes. At least this is done in Germany; in England the acid obtained is usually too weak. Deacon and Hurter (Pat. 2,311, 1888), therefore, now pass the gases up a tower filled with flints, in which Weldon mud is run down, which absorbs the hydrochloric acid with evolution of chlorine.

The gases can now be employed directly for making bleach liquor or chlorate liquor from milk of lime. If, however, bleaching powder is to be made, they must be freed from water by passing them through a lead tower packed with coke, in which sulphuric acid of not less than 140°Tw. is kept trickling down. The removal of water is very necessary for dealing with this gas, which, owing to the great excess of nitrogen and oxygen present, contains at most 10 p.c. of chlorine, and cannot be absorbed in ordinary bleaching-powder boxes, but must be treated in apparatus specially constructed for this pur-

pose (*cf. infra*). In winter it is easier to dry them than in summer, so that it is also easier to make strong bleach; but this can be done in summer time as well by employing sulphuric acid of 150°Tw., of which each apparatus requires 5 to 6 tons per twenty-four hours.

The results to be obtained by Deacon's process are stated a little differently by various manufacturers, which cannot excite any surprise, as so much depends upon care and skill. Hurter (S. C. I. 1883, 109) states that he obtains for every 50 tons of salt passed through the decomposing pans 17 to 18 tons of bleaching powder with a decomposer of average activity. Eschellmann (S. C. I. 1883, 108) gives an average of 18 tons of bleaching powder for every 54 tons of salt-cake, that is, 1 ton of bleach for 54 cwt. of salt. Weldon (S. C. I. 1883, 108) gives 1 ton of bleach to 60 cwt. of salt.

All this does not include the roaster-acid and that condensed before and after the decomposer; by utilising this in a Weldon apparatus, another 6 to 7 tons of bleach can be obtained.

The heating of the apparatus requires 8 to 10 cwt. of coal per ton of bleach. The total consumption of coal (including the concentration of the sulphuric acid employed in the drying tower?) does not exceed the weight of bleach produced.

The amount of wages for attending to the superheating and decomposer, for slaking lime, charging the chambers, packing the bleach, and preparing the contact substance, averaged, in 1883, 14s. to 15s. per ton of bleach.

During the first years of its existence, the Deacon process had to contend with many drawbacks, principally owing to two circumstances. Firstly, the contact substance frequently did not yield satisfactory results; its renewal caused very awkward delays, and the redipping mostly did not sufficiently revive its former activity. This has been overcome in the way stated above, by systematically changing the contact substance and throwing it away as it comes out of the decomposer. Secondly, the Deacon gas formerly owing to the cubical shape of the decomposer, which did not prevent fire-gases from being drawn into it, frequently contained very much carbonic acid, which spoiled the bleaching powder, so that most works could only produce weak bleach. This has also been entirely remedied by making the decomposer in the form of a cylinder, thus avoiding a large number of joints and inconvenience in expansion and contraction.

All the difficulties which formerly impeded the success of the Deacon process have been overcome long since, and although it still requires very careful handling, it is now quite under control. Its great advantages are, firstly, the very superior yield of chlorine, secondly, the fact that there cannot possibly be a nuisance caused by it, all the gases being drawn through the apparatus, so that the pressure within is below that of the atmospheric air.

The reason why, in spite of this, the Deacon process has come to a comparative standstill (it is in work in about 4 English, 2 German and 2 French works) seems to be that it requires a great deal of capital outlay, which most manufacturers do not like to incur during the depression of prices in the alkali trade, and while several other new

chlorine processes seem to be on the eve of attaining an even greater measure of success.

Hargreaves, Robinson, and Hargreaves (E. P. 5,673, 1884) propose, as an improvement, to mix HCl gas, whilst hot, with a small quantity of copper chloride vapour, and to pass it through the Deacon apparatus, by which means the rate of decomposition is increased. The chlorine formed is passed into a bleaching-powder chamber of special construction, containing mechanical agitators, along with some strong chlorine, obtained by absorbing some of the weak chlorine in milk of lime and liberating the Cl again by HCl in stone stills.

**Chlorine produced from hydrochloric acid and air by other contact substances.** Many such substances have been the objects of proposals, some of which are inseparable from the manufacture of chlorine from metallic chlorides, that is from HCl in the nascent state. A general investigation on the mutual action of HCl and O in the presence of certain metallic compounds (of Cu, Fe, Mn, and Cr) has been made by Lamy (Bl. 1873, 20, 2). We must refer to the original, and will only mention that he found copper salts much more efficient than others, and that with these the decomposition is at its maximum at about 440°.

The proposals to employ ferric chloride (Thibierge, 1855, and others), or chromic oxide (Hargreaves and Robinson, 1872) have not had any practical success.

Nickel oxide has been proposed by L. Mond (E. P. 8,308, 1886). He passes HCl over heated NiO, when the chlorine combines with the base. The product is then in the same apparatus exposed to dried and heated air, whereby NiO is reformed and Cl is given off. In order to increase the active surface, pumice stone is impregnated with the chloride, and after drying the mass is exposed to the action of the gases in cylinders made of earthenware or enamelled iron. The gaseous HCl and air being previously heated, the retorts do not require very much additional heat from without, and therefore can be made of a large diameter. It is claimed for this process that it converts the HCl completely into chlorine, and that impure HCl, which is unfit for the Deacon process, is here quite suitable.

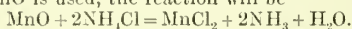
**Chlorine from the residual liquors of the Ammonia-Soda process.** The principal, undoubtedly at present the only reason, why the ammonia-soda process has not superseded the Leblanc process, is the fact that the chlorine of NaCl in the former process goes to waste in the form of CaCl<sub>2</sub>. Very numerous processes have been proposed and tried to avoid this loss by preparing HCl or free Cl from the liquors of the ammonia-soda process. We shall here only treat of those processes by which free chlorine is obtained.

1. *Chlorine from ammonium chloride.* Instead of first decomposing NH<sub>4</sub>Cl by lime, and thus obtaining NH<sub>3</sub> and CaCl<sub>2</sub>, Mond proposes to recover chlorine directly from NH<sub>4</sub>Cl, of course along with ammonia (D. P. 65, 66, 1,018, 1,049, 3,238, all of 1886). The solution of ammonium chloride is boiled down to dryness; the dry NH<sub>4</sub>Cl is volatilised and the vapour is passed over nickel protoxide heated to about

400°, or combinations of NiO with fixed acids (silicic, phosphoric, boric, &c.) at a somewhat lower temperature. The chlorine then combines with the NiO, forming an oxychloride, while the ammonia passes on and can be utilised in any convenient manner. The oxychloride is now treated, either with superheated steam of 450°, or with dried air heated to 500°C. In the former case HCl, in the second free Cl, is given off (forming 5 to 7 p.c. of the escaping gases), whilst NiO remains behind and can be used over again for the first process. As some NH<sub>3</sub> remains behind at the first stage, which would be destroyed in the second, it is to be recovered by the aid of a vacuum, or by driving it out by means of an inert gas.

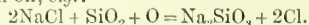
For carrying out this process, a number of cast-iron retorts are set obliquely in one common furnace, and heated by direct fire, or by generator gas. The retorts pass through the walls of the furnace at both sides, and are at each end provided with covers and openings for the inlet and outlet of the gases. Since cast-iron is too much acted upon, the retorts are to be enamelled or lined inside with fire-clay, graphite, carbon, &c.

The Verein für chemische Industrie at Mainz (E. P. 3,322, 1886) passes the vapours of ammonium chloride over any oxide of manganese, at a temperature not reaching red heat. If MnO is used, the reaction will be



If now air is passed over the resulting MnCl<sub>2</sub>, MnO and Cl are obtained;  $\text{MnCl}_2 + \text{O} = \text{MnO} + 2\text{Cl}$ .

*Chlorine from calcium chloride.* Lalande and Prud'homme (Bl. 17, 290; 26, 74) showed that, if alkaline or earthy chlorides are mixed with silica, boric, stannic, phosphoric acid or alumina, if this mixture is made red-hot, and dry air is passed over it, then chlorine is given off, e.g.:



It has long been known that chlorides are decomposed by silica or silicates in the presence of steam, and that HCl can be got in this way, but so far as the manufacture of hydrochloric acid is concerned, the expense of this process must be always too great (*cf.* Hurter, S. C. I. 1883, 105). It may be different where the direct production of chlorine is aimed at.

E. Solvay (Patents No. 77, 1877; No. 838 and 839, 1880; No. 7,258, 7,259, 7,266, 8,724, of 1885; 13,389, of 1886) mixes the chlorides with silica, alumina, or clay, and exposes this mixture to a current of dry air at an intense heat; silicious clays or infusorial earth are much preferable to sand. The silicious substances used are first freed from CO<sub>2</sub> by acid treatment, and are used in such excess that the mixture does not fuse. The air used is purified from moisture and CO<sub>2</sub>. The iron vessels used are covered with preservative coatings of certain mixtures of soda, clay, and vitrifiable products. There is also a cupola furnace mentioned, the waste heat being employed for heating up the air by means of a recuperator. The last patent describes a continuous furnace, consisting of a series of hollow vertical columns of small diameter, made of fire-proof material, so constructed that all parts can freely expand or contract. These columns are heated from the outside by means

of a gas-producer. The matter to be heated is put in at the top, and the decomposed matter is continuously drawn out at the bottom; air previously dried and heated is admitted at the bottom and is drawn away at the top of the column, charged with chlorine.

The residue from this operation was formerly proposed to be utilised for the manufacture of cement. It is now proposed to use this substance, consisting of CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, with solid NH<sub>4</sub>Cl and heat the mixture to 350°C., when all NH<sub>3</sub> is liberated and there remains an intimate mixture of CaCl<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, well adapted to evolve chlorine under the influence of air and heat. The same silica and alumina may thus be used over and over again.

Twynam (E. P. 731, 1885) first forms an oxychloride by adding lime to the CaCl<sub>2</sub> liquor, and subjects this to the action of air and heat.

Tagnet (G. P. 30,839) heats the dry residue from CaCl<sub>2</sub> liquor with pure silica and MnO<sub>2</sub>.

*Chlorine from magnesium chloride.*

It is well known that MgCl<sub>2</sub> is much less stable than CaCl<sub>2</sub>; on evaporating its solution beyond a certain point it begins to give off HCl, and this is continued while the mass is being dried and calcined. The result is, however, not a mere splitting up of MgCl<sub>2</sub> + H<sub>2</sub>O into MgO + 2HCl, but there is always a considerable formation of oxychloride, and there are, moreover, great practical obstacles to the carrying out of this reaction for the recovery of HCl. Passing steam over the mass during the heating greatly facilitates the evolution of HCl, and ultimately there may be thus a practically complete decomposition into MgO and HCl, but the expense of this process is too great, and the hydrochloric acid made in this way is too dear. As in the case of CaCl<sub>2</sub>, the problem seems to offer much more chance of success, if the direct production of chlorine is aimed at, by passing heated air over MgCl<sub>2</sub>, either by itself or mixed with some substance intended to facilitate the reaction.

In his patent of 1872 Solvay had proposed to employ MgO instead of lime for decomposing the ammonium chloride liquors of the ammoniasoda process, and recovering MgO and HCl from the MgCl<sub>2</sub>. This, we have seen, can hardly be expected to pay; therefore the direct production of Cl from liquors obtained in this kind of manufacture has been the object of further attempts. In pursuance of these, the magnesium chloride obtained from the mother liquors of sea-salt making, and especially that resulting in enormous quantities in the Stassfurt potash industry, has been brought in for the same object.

We have already mentioned the processes of Lalande and Prud'homme, and that of Solvay, of 1887, which apply to MgCl<sub>2</sub>, as well as to CaCl<sub>2</sub>. Some other proposals are those of Ramdohr (1882) and J. Townsend (1881).

The most persistent efforts in this direction have been made by Weldon, who was later on joined by Péchiney.

In 1872, simultaneously with Solvay's just-mentioned plan, Weldon brought out his 'magnesium manganite' process, which was actually carried into practice a few years after, but abandoned again. It consisted in boiling down the mixed solutions of MgCl<sub>2</sub> and MnCl<sub>2</sub> to dryness,



and then calcining the mass in the presence of air. Here HCl and Cl are given off, and the residue is a compound of MgO with MnO<sub>2</sub>, which is treated for chlorine in an ordinary Weldon still.<sup>1</sup>

We have thus a combination of the MgCl<sub>2</sub> process with the manganese recovery, more intended for the latter than for the independent working up of MgCl<sub>2</sub>.

This process was tried on an industrial scale, as well as the simple decomposition of magnesium chloride by heat, at the Gerard's Bridge Works at St. Helens, but had to be abandoned because the furnace-beds were too quickly destroyed by the MgCl<sub>2</sub> solution penetrating into them. This led Weldon, in 1881, to the idea of adding to a concentrated solution of a chloride or mixture of chlorides, the oxide of the same metal or metals, and then treating by heat and air solid masses of the mixture.<sup>2</sup> This improvement is embodied in the patents No. 964 to 968 of 1881. One of these already embodies the plan of working with an oxychloride of magnesium formed by adding magnesia to a very strongly concentrated hot solution of MgCl<sub>2</sub> in such proportions that a hard solid mass is obtained which does not appreciably soften when heated. From 1 to 2 equivalents of MgO are generally sufficient for a solution containing 6H<sub>2</sub>O to 1MgCl. The resulting oxychloride is now heated in a current of air in a specially constructed furnace.

This process was taken up by Messrs. Péchiney & Cie., of Salindres, and has received a great many improvements in the course of being worked out on a large scale, for which credit is to be given to M. Péchiney and his engineer M. Boulouvard. These improvements refer partly to apparatus and partly to changes in the procedure. (Patents No. 4,079 and 5,868, 1883; 9,304, 9,305, 9,306, 9,307, 9,688, 11,035, and 11,036, of 1884; 9,227 and 9,831, of 1885.) In the course of these labours it turned out that probably the principal importance of that process would lie, not in its application to the liquors of the ammonia-soda process, but in producing chlorine from the enormous quantities of magnesium chloride obtained in a concentrated solution as a hitherto worthless by-product of the manufacture of potassium chloride at Stassfurt.

The process as it was carried out at Salindres in the latter part of 1887, on an experimental scale of  $\frac{3}{4}$  ton of chlorine per day, has been fully described, with many illustrations, by Dewar (S. C. I. 1887, 775). We here give only a summary of that description, as no doubt further improvements will be made (and have indeed been promised) before the process is made to work on a larger scale, a plant corresponding to 6 tons of chlorine per diem having been taken into hand.

**First operation.**—Magnesia is dissolved in HCl. This magnesia is a portion of that which results from the fifth operation; the HCl results in part from the same operation, and the remainder from the decomposition of salts. (Where MgCl<sub>2</sub> is the starting-point this operation is of course left out.) There is in this

operation a considerable rise of temperature and a tendency of the mass to boil over. This is prevented by slowly running HCl into a well, similar to the neutralisers in Weldon's old process, adding the magnesia little by little, and stopping the operation for a short time whenever the heat approaches the point of ebullition. Lastly, enough MgO is added to precipitate part at least of the foreign oxides (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>), and a little CaCl<sub>2</sub>, to transform part of the MgSO<sub>4</sub>, resulting from the sulphuric acid contained in the hydrochloric acid employed.

**Second operation.**—Preparation of the magnesium oxychloride. The clarified liquor resulting from the first operation is evaporated down to the point at which it contains no more than about six equivalents of water, and is now converted into oxychloride in an annular sheet-iron vessel, slowly revolving on rollers on a horizontal plane, three mechanical stirrers keeping the mass agitated. Here magnesia, about 1 $\frac{1}{4}$  eq. per eq. of the MgCl<sub>2</sub> employed, is gradually mixed with the latter, whereupon, with evolution of much heat, the mass solidifies in the form of pieces of different sizes. This oxychloride contains 35.00 MgCl<sub>2</sub> (= 26.16 p.c.), 19.84 MgO (= 1.346 eq. of the MgCl<sub>2</sub>), 41.16 H<sub>2</sub>O, 4.00 impurities.

**Third operation.**—Breaking, crushing, and sifting the oxychloride. It should be reduced to pieces not larger than a walnut, but free from dust. The latter is sifted out, and can be reintroduced into the first or second operation.

**Fourth operation.**—Drying the oxychloride of magnesium. The less water it contains the more free chlorine and the less HCl will be formed in the decomposition by heat and air. The temperature in drying must, however, not exceed 250° to 300°C. Since dust must be avoided, the drying cannot be promoted by mechanical agitation, but it is done on a train of wagonettes, with shelves one above the other, on which the oxychloride is spread in layers of 5 to 6 centimetres thickness, and which circulate in a flue in a direction opposite to that traversed by the hot gases. The filling of the wagonettes is performed by a mechanical apparatus. During this operation the oxychloride loses 60 to 65 p.c. of its water, and it disengages 5 to 8 p.c. of its chlorine in the state of HCl. Thus 100 of original oxychloride is reduced to 73.36, the raw product containing p.c. 41.45 MgCl<sub>2</sub> (= 33.30 Cl), 28.36 MgO (= 1.511 eq. per eq. of MgCl<sub>2</sub>), 21.62 H<sub>2</sub>O, 5.47 impurities. The drying has thus caused a loss of 6.6 p.c. of the chlorine originally present. This loss will hardly exceed 8 p.c.

**Fifth operation.**—Decomposition of oxychloride by heat and air. This takes place in a set of furnaces consisting each of four narrow perpendicular decomposing chambers, 3 × 1 × 0.08 metres inside, having very thick walls. These furnaces are, each in its turn, heated up to a bright red heat by connecting them with a movable regenerative burner fed with gaseous fuel. When the proper temperature has been reached, the burner is disconnected and moved on to the next furnace, whilst the first furnace is charged with about 8 cwt. of magnesium oxychloride in small pieces. This substance is now rapidly

<sup>1</sup> Details in Lunge's Alkali, 3, 237–247.

<sup>2</sup> This idea has again been patented in a slightly modified form by J. Wilson, No. 3,098 of 1885.

heated by the heat stored up in the walls of the furnace, a current of heated air traversing the chambers at the same time, so that decomposition ensues, and a mixture of gases and vapours containing both HCl and free chlorine passes away along with unconsumed air. The residual oxide remaining at the end, and containing from 15 to 19 p.c. of the chlorine charged, is drawn out, and the chambers are now ready to be again connected with the regenerative burners to be heated up for a second operation.

The issuing gases contain from 81 to 85 p.c. of the chlorine charged, of which slightly more than half is in the state of free Cl, the remainder as HCl.

The maximum percentage of chlorine in the gases is from 6.25 to 7.78. They are drawn off from the furnace by means of an apparatus consisting of two bells plunging into a solution of calcium chloride and alternately moving up and down, so that the action is a continuous one. This aspirator acts at the end of the condensing apparatus interposed between itself and the furnace. The condensing apparatus consists of three parts:—1. A refrigerator consisting of a stone tower, in which are arranged, in an inclined position, glass tubes through which cold water is kept flowing. Here most of the water, with but little HCl, is condensed. 2. A set of stone 'bombonnes.' 3. An ordinary condensing tower packed with coke. The HCl is completely condensed, the mixture of products from all three apparatus forming an acid of about 18° Tw. The residual gases containing all the free chlorine are at present utilised by being absorbed in milk of lime for the manufacture of chlorates.

The final result is at present that, of 100 parts of chlorine put in work, there is:

Lost in the various manipulations . . . . .	5.00	
Lost in drying . . . . .	6.37	
	—	11.27
Entering again into the process:		
Remaining in the residues . . . . .	13.30	
Condensed in the state of HCl 35.29		
	—	48.59
Produced as free chlorine . . . . .	40.14	
	—	100.00

It is believed that the loss of Cl can be diminished, and the proportion of free chlorine can be increased, by greatly increasing the temperature of the furnace, which at present is about 1,000°C.

In the original paper there are detailed calculations concerning the present and the probable future cost of chlorine by this process which we leave out, as they must necessarily be overtaken by the facts before this is in the hands of readers. The upshot of the whole is that the natural place for the adoption of this process is Stassfurt, which would then almost monopolise the chlorine trade.

The most recent patents referring to the manufacture of chlorine from magnesium chloride are those of Heinzerling and Schmid (G. P. 41,996); Konther (G. P. 41,351); Kingzett (S. C. I. 1888, 292); Schloosing (Pat. 11,821, 1887); Branley (Pat. 8,289, 1887); Mond and Eschellmann (Pat. 17,273, 1887); Solvay (G. P. 44,865). A very complete synopsis and criticism of the

recent processes for manufacturing chlorine (and hydrochloric acid) by means of magnesium chloride has been given by Eschellmann (C. I. 1889, 2; comp. *ib.* p. 100).

*Various proposals for the manufacture of chlorine.*—Chlorine, by the action of air on heated chloride of iron or on a mixture of sulphide with common salt, has been frequently patented—Thibierge, 1855; Macfarlane, 1863; Longmaid, 1815; Swindells and Nicholson, 1852; Deacon, 1871.

*Chlorine produced by passing HCl gas over heated peroxide of iron or manganese* is the subject of a patent by H. Burns, No. 15,418 of 1886.

*Chlorine by permanganates* has been the object of patents by Tilghman (1847), Condy (1866), Tessié du Motay (1871 and 1873).

*Chlorine from chromates* and HCl has been proposed to be made by MacDougall and Rawson (1848), Peligot (A. Ch. (2) 411, 267), Gentile (1861), Shanks (1858), Claus (1867), Aubertin (1873).

*Chlorine by heating metallic chlorides with MnO<sub>2</sub> and SO<sub>2</sub>H<sub>2</sub>* was patented by Binks in 1853.

*Chlorine by the assistance of nitric acid or nitrates.* Baggs and Simpson (1864) proposed making chlorine from aqua regia. Dunlop (1847) patented the preparation of chlorine along with nitrous acid, by heating together common salt, nitrate of soda, and sulphuric acid; the nitrous acid is absorbed by vitriol and the chlorine is passed on to bleaching-powder chambers. This process has been working for many years at St. Rollox; it was patented again by Roberts and Dale in 1868, and a patent running on similar lines is that of J. Taylor (No. 13,025, 1884).

Other processes employing nitrates or nitric acid, which have not had any practical success, are those of Banks (1839), Tessié du Motay (Bl. 22, p. 48), Schlösing (C. R. 55, 284). The newest patents are those of MacDonald, No. 62, 1887, and Just, No. 14,857 and 14,859, of 1888.

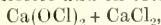
*Chlorine by the electrolysis of sodium chloride* has been the subject of many proposals. We only mention the patents of C. Watt (1851), Dickson (1862), Fitzgerald and Molloy (1872), Berger-Spence, and Watt (1882), Geisenberger (1883), Richardson and Grey (1884). Naudin and Bidet (Bl. 40, 214) have made a scientific investigation of this process, which does not at present offer any prospects of success, so far as the actual manufacture of chlorine compounds is concerned. It may possibly be different with the direct utilisation of the nascent chlorine for bleaching purposes, but these processes (which are equally in the experimental stage) do not belong to the present section. About L'Hermite's process which produces a bleaching liquor from magnesium chloride by electrolysis, *v. infra*.

*Chloride of lime or bleaching powder.* By far the greatest part of the chlorine produced on a manufacturing scale is converted into *chloride of lime* or *bleaching powder*. Otherwise most of the hydrochloric acid produced in the process of decomposing common salt by sulphuric acid would be wasted; that portion of it which would be required by those preparing chlorine for bleaching purposes &c. would cost any consumer not in the immediate neighbour-

hood of the works much more than the finished chloride of lime does now.

The first to suggest the industrial application of chlorine to bleaching was Berthollet, in 1785, and in 1789 was produced the liquor called 'Eau de Javel,' manufactured by passing chlorine into a solution of potash. This for the first time enabled the bleacher to buy his chlorine in an available form, but it was too dear for most purposes, and so was the kindred liquor made from soda. Both, especially the latter, have still some application in special cases, but their part is very small in comparison to that played by the analogous compound, manufactured with the cheapest of all bases, lime. The use of this was first suggested by Charles Tennant in 1798, and this was all the more important as the alkalis were at that time enormously dearer than they are at present. At first Tennant used milk of lime, and thus obtained the solution known under the name of 'bleach-liquor,' and extensively manufactured even now. In 1799 he took out his patent for absorbing chlorine by dry hydrate of lime, and the compound thus formed, 'bleaching powder,' was sold by the St. Rollox Works, established in the same year, at 140*l.* per ton.

*Composition of bleaching powder.*—The union of chlorine and lime seems to take place in a very direct way, and the composition and many of the properties of the new substance formed also seemed to favour the assumption that it was merely a compound of  $\text{CaO}$  and  $\text{Cl}_2$ ; the name 'chloride of lime' was given to it on this assumption. Long before our present theories made it unlikely that  $\text{CaO}$  could combine as such with chlorine, Balard, in 1835, propounded the theory that bleaching powder was a compound or mixture of equivalent proportions of calcium hypochlorite and chloride



mixed with an excess of calcium hydrate. This theory, supported by Gay-Lussac in 1842, in point of fact explains nearly all the properties of bleaching powder, and does so entirely, if the combination between the hypochlorite and the chloride is understood to be not a mechanical mixture, but a real compound, which, according to our present theories we must regard as  $\text{Ca} \begin{smallmatrix} \text{Cl} \\ \text{OCl} \end{smallmatrix}$ , that is, calcium combined with the negative radicals of both chloride and hypochlorite; the latter salts, however, do not yet exist as such in the dry state, but are only formed when the compound is brought into contact with water, 2 molecules of  $\text{Ca}(\text{OCl})\text{Cl}$  splitting up into 1 of  $\text{Ca}(\text{OCl})_2$  and 1 of  $\text{CaCl}_2$ . This view, first mentioned (without substantiating it) by Odling, has been very strongly supported by the investigations of Lunge, carried on with Schäppi and Naef in the years 1880–1884, which proved that calcium chloride as such does not form a constituent of dry bleaching powder, and that the excess of lime always found in it can be reduced to so small a quantity that none of the theories formerly advanced in order to explain the constant presence of such excess of lime can be upheld.<sup>1</sup>

<sup>1</sup> The literature on the constitution of bleaching powder previous to 1880 is collected in Lunge's *Sulphuric Acid* and

*The preparation of lime for bleaching powder.*—The lime intended for manufacturing bleaching powder must be made from as pure a limestone as possible, and should be most carefully burned. The Tyneside manufacturers burn it themselves, mostly from Rouen cliff (which is brought to the Tyne as ballast in colliers). In Lancashire it is obtained ready burnt from Buxton; this lime, on slaking, leaves all the unburnt pieces behind. Lime containing clay gives badly settling bleach; iron and manganese colour it; magnesia seems to interfere with its stability. Bleach made from 'fat' lime keeps much better than that made from poor lime.

Where the bleach manufacturer burns his own lime, it is generally not done in ordinary lime-kilns, but in horizontal furnaces where the fuel is kept apart from the lime. Gas producers are very useful for this purpose.

The burning ought to be continued so long that the lime contains less than 2 p.c.  $\text{CO}_2$ . If, however, the burning is overdone, the lime is 'dead,' it slakes badly and is no more fit for making bleach than underburnt lime. The lime-kilns mostly used by the Tyne bleach manufacturers hold about 10 tons and require 5 tons of coal for burning. The burning takes 4 days, after which the openings are well plastered up and the kiln is allowed to cool down for about 2 days before taking out the quicklime.

The burnt lime is slaked by spreading it on a brick floor and gradually sprinkling water over it till it has completely fallen to powder, after which, it is occasionally turned over. All unburnt or unslaked pieces must be taken out, and the whole must be sifted through a revolving sieve covered with wire-gauze of 25 holes per linear inch. The finer the lime is sifted the better it absorbs the chlorine. The hydrate of lime is kept in an air-tight place till it is perfectly cool, during which time any unslaked particles will also be converted into hydrate.

Calcium hydrate contains 24.5 p.c. of water, and the product prepared as above ought to approach this composition as nearly as possible; in winter it may contain 0.5 p.c. more. Only then will the strongest bleaching powder be obtained. This is the experience obtained at Aüssig, but it appears that in Lancashire, both for Weldon and Deacon bleach, there is as much water used as will allow the hydrate to be sifted (from 24.5 to 27 p.c.).

*The bleaching-powder chambers.*—The chambers or 'boxes' in which the lime is exposed to the action of chlorine were formerly often made of tarred wood, masonry, or stone flags, the latter being frequently provided with shelves inside. For the ordinary strong chlorine gas, these have been in England universally replaced by large chambers of about 6½ ft. in height, so that a man can work inside them, of a width of from 10 to 20 ft. and more, and up to 100 ft. long. Their sides and top are usually made of 5 or 6 lb. sheet lead, fastened by straps

Alkali, 3, 91–112; of later papers, apart from those mentioned above, we quote Lunge and Schäppi, D. P. J. 237, 63; Chemische Industrie, 1880, 216; Kraut, A. 214, 354, and 221, 108; Lunge and Naef, A. 219, 129; Lunge, A. 223, 106; T. O'Shea, J. C. S. 43, 210; Dreyfus, Bl. 41, 609; Lunge and Schoch, Ber. 1887, 1, 474.



on a timber frame-work, exactly like vitriol chambers. In Lancashire they are frequently made of cast-iron flanged plates bolted together, and protected by oil-paint against the action of the gas; but these chambers are more expensive, and are apt to contaminate the bleach with iron; they are also difficult and costly to repair. On the Continent chambers made of stone flags, *e.g.*, of volvic lava, are still frequently met with.

The floor is made of large stone flags, or of coal-tar asphalt, the joint between the sides and the edge of the floor being specially protected by a skirting board and asphalt poured behind it.

The chambers must be fitted with doors (generally made of iron protected by paint), with glass panes in two opposite doors for observing the colour of the gas, with 'lutes' for introducing the gas, and with some contrivance for removing the gas remaining at the end of the operation (*v. infra*).

It is preferable not to erect the chambers on the ground-level, but upon pillars, like vitriol chambers, leaving about 10 ft. of clear space from the ground. In this case the packing of the finished bleach into casks can be done without the men entering the chamber, by means of trap-doors in the chamber-floor, with wooden hoppers attached underneath, below which the casks are placed, the bleach being pushed down into them from without by means of wooden rakes.

Sometimes several chambers are combined to form sets, so that the gas always enters first into a nearly finished chamber, and the excess-gas into a freshly charged chamber, where it is entirely taken up.

Jahne (D. J. 283, 287; S. C. I. 1887, 367) gives a number of observations made with a set of four chambers connected in this way.

Many proposals have been made for mechanical absorbing apparatus for chlorine (Lunge, *l.c.* 164-165), but none of them seems to have met with permanent success; sometimes the working parts are worn out after a short time, and sometimes the bleach produced in them is too weak. Of course it cannot be said that the construction of a mechanical chlorine absorber for dry lime is an impossibility, but it must be difficult to construct unless a perfectly regular stream of chlorino gas is at command and efficient means are employed for artificially removing the heat given off during the absorption. New apparatus for the treatment of gases by solids have been patented by Mond (G. P. 45,740) and Hasenclever (Pat. 17,012, 1888).

The manufacture of the bleaching powder in the chambers takes place in this way. The hydrated lime is spread upon the floor in a layer of 3 or 4 inches in depth; its surface is drilled into furrows by means of a wooden tooth-rake, to assist absorption. All joints are plastered up with lime-putty, and the gas is admitted, leaving at first an air-hole open, which is only closed when chlorino issues from it. The gas is at first very quickly absorbed, as may be seen by its colour when looking through the glass-panes, afterwards much more slowly. If there is not sufficient care taken to keep it free from acid and moisture, lumps are formed which are very injurious. Towards the end an excess of gas

must be put into the chamber, and on this account it is preferable to lessen the pressure by connecting the first chamber with a second one charged with fresh lime.

When the lime will not absorb the chlorine as fast as it enters the chamber, this is left to itself for 12 hours, or better still for 24 hours, after which time the chlorine will nearly always have been absorbed.

It is difficult to get full strength bleach by one operation; there is always a superficial crust which prevents the gas from penetrating right through. It is therefore necessary to turn the stuff over with spades, and drilling the surface again, whereupon the treatment with gas is repeated. Sometimes this must be done even a third time, before the appearance of the product and the laboratory test show it to be finished. It ought then to consist of pretty heavy flakes, easily crushed, but not dusty, which can be kneaded with the fingers into a tough paste. The laboratory test of a sample carefully taken from various parts of the chamber ought to be at least 36 p.c., better 37 p.c., as the bleach loses at least 1 p.c. in packing. With impure, badly burnt, badly slaked, or badly sifted lime, with moist chlorine or such as contains carbon dioxide, no strong bleach can be expected, and when trying to force this by 'gassing' too much, it will be found that the strength actually goes back, calcium chlorate and chloride being formed.

As it is indispensable to employ an excess of chlorine in order to finish the bleach, there must be always a great quantity of unabsorbed gas in the chamber at the end, and if no special precautions are taken in this respect, the opening of the doors will cause an intolerable nuisance. This ought to be prevented in any case. It can be done by drawing the gas out of the chamber, either by chimney draught or by mechanical means, and making it to pass through a milk-of-lime or even through a hydrate-of-lime absorber.

Probably the best means for this end is the plan patented by Brock and Minton (E. P. 7,199, 1866; comp. 23rd Report on Alkali &c. Works, 58-60) who, before opening the door, sprinkle lime into it by means of a wooden hopper and fan fixed in the roof, in such quantity that the free chlorine is entirely absorbed without bringing down the strength of the chamber below the required point. There is thus also an additional yield of bleach. Lime in fine powder is put into the hopper fixed in the roof of the chamber, and is admitted into the latter by means of a valve. A vertical shaft, inside a box between the hopper and the valve, is made to turn by a handwheel, and, being armed with blades, forms a fan or distributor, which draws air from the chamber, mixes it with the descending lime, and causes this to pervade every part of the chamber. One such machine is sufficient for a chamber of 100 ft. length, but generally three are provided. This treatment reduces the amount of chlorine in the chamber-air to less than 1 grain per cubic foot (0.82 on the average), without materially reducing the strength of the bleach, which at Messrs. Sullivan & Co.'s Works still tests 37.5 to 38 p.c. *after packing*. For a chamber of 10 tons bleach, finished with a considerable excess of chlorine, 4-5 cwt. of

lime dust are thrown in, which produce 6 cwt. of bleach. It requires an hour or two to settle, but the whole of the operation is completed in 3 hours. The doors can then be taken down without any strong smell being perceptible within a few feet of the chamber, and packing can at once be proceeded with. The extra bleach produced much more than pays for the treatment.

For testing the amount of chlorine in the air of bleaching-powder chambers previous to opening the doors, several kinds of apparatus have been proposed—*e.g.* that of Ballard (21st Report on Alkali &c. Works, 37; 22nd do. 55) and of Stark (S. C. I. 1885, 311). Ballard's apparatus consists of a cylindrical glass jar, closed at the top by an indiarubber cork through which the nozzle of a 4-ounce enema ball (finger pump) passes, as well as an elbow tube reaching down to the bottom. The lower end of this tube is closed at the lamp so as to leave an opening fine enough for a needle only to pass through. The horizontal branch of this tube is inserted in the side of the chamber at a point about two feet from the bottom. When compressing the ball, the air is driven out by a small hole made in the nozzle just above the cork; this is now closed by the finger, and on relaxing the pressure the ball will expand, and will cause 4 ounce measures—that is,  $\frac{1}{2}$  of a cubic foot—of chamber-air to enter into the jar and bubble through the test solution contained therein. This is continued till the end of the reaction is indicated by the test-liquor turning blue. The latter consists of 3·185 grains of arsenious acid, dissolved in sodium carbonate and rendered neutral by sulphuric acid, 250 grains potassium iodide, 50 grains precipitated chalk, 10,000 grains of water, 6–10 drops ammonia. For each test 400 grains are used, adding a little starch paste at the time of using. When  $2\frac{1}{2}$  grains of chlorine per cubic foot is present in the chamber-air, ten aspirations of the chlorometer will cause a blue colour to appear; if more aspirations are needed, there is less chlorine present and *vice versa*. Stark's apparatus attains the same end, not by the finger pump (which is certainly a somewhat rough instrument), but by a gas-burette on the Orsat principle.

The following rules are recommended by the Chief Inspector of Alkali &c. Works (Mr. A. E. Fletcher), in his twenty-first Report, p. 12:

I. Bleaching-powder chambers should contain not less than 200 square feet of floor space for every ton of powder made in them per week. If there is less space the work, and especially the packing, must be hurried too much.

II. The chambers should be so arranged and connected together that the residual chlorine from a finished chamber may be drawn into one containing fresh lime, unless some other means be employed for absorbing it (such as Brock and Minton's plan described above). The air finally discharged into the atmosphere or into a flue or chimney must not contain more chlorine than  $2\frac{1}{2}$  grains per cubic foot.

III. No chamber should be opened when the air in it contains more than  $2\frac{1}{2}$  grains of chlorine per cubic foot. In testing for this, the air should be drawn from a point not more than

2 feet above the chamber floor, and taken from the draught end.

IV. No chamber may be opened until the air in it has been tested, and the result of such test entered in a book.

V. No chamber may be opened except in daylight.

It is very important to prevent the temperature from rising too much during the absorbing process. Contrary to some assertions, bleaching powder is all the better the cooler the chambers are kept. For this reason lead or iron boxes are preferable to brick or stone chambers, and it is always easier to make strong bleach in winter than in summer. It is stated that, even during the heat of summer, strong bleach can be made by diluting the chlorine with 50 p.c. of air by means of an air-pump; in this case the rise of temperature is never too high, there is no crust formed on the top, and the bleach can be regularly kept at 38 p.c. This is also the object of a patent by Opl (G. P. 23,587, 1883), who uses chambers cooled by water from the outside, as well as diluted and specially purified chlorine, for making the strongest bleach.

*The absorption of weak chlorine*, that is, chlorine diluted with very much nitrogen and oxygen, as it is obtained in the Deacon process, and in most of the processes proposed for dealing with calcium and magnesium chlorides, cannot be carried out in the ordinary chambers. The most efficient plant for this purpose seems to be that worked out by Deacon himself. The absorbing space is immensely increased, and at the same time the process is made a continuous operation by employing a large number of chambers, each of them provided with a number of shelves, and connecting them in such a way that the fresh chlorine gas always enters the chamber in which the bleach is nearly finished, and the last gas, then containing only traces of chlorine, is passed through a chamber just charged with fresh lime. These chambers cannot very well be made of any other material than of stone, slate, sandstone flags, volcanic lava, &c. The distributing pipes are of cast iron. The chambers are arranged in pairs, the gas being made to pass down the one half and up the other half of the pair.

Practically a set of Deacon chambers for producing 25 tons of bleach per week consists of seven double chambers with sixteen shelves each, with a total area of 1,250 square feet, upon which  $18\frac{1}{2}$  cwt. of calcium hydrate can be laid  $\frac{5}{8}$  inch deep (which is the greatest thickness practically applicable in this case). Every sixteen hours one of the pairs of chambers comes in turn to be drawn and recharged. Hurter (D. P. J. 223, 200, 417; 224, 424) has proved that it is more advantageous to convey the gas in a downward than in an upward direction. He has also shown that such chambers would not be applicable to strong chlorine, as then the temperature would rise to 70° or 80° C., but in the present case the inert gases, of which there are about 90 p.c. present, prevent the temperature rising to any hurtful extent.

Solvay (E. P. 7,259, 1885) treats the dilute chlorine obtained from his process from calcium chloride, by placing the lime in a layer of suitable thickness on beds of porous mineral matters,

such as pebbles or asbestos cloth, and causing the diluted chlorine to pass downwards through the same. If the gases pass upwards, channels are soon formed and irregularity ensues.

The yield of bleaching powder may be taken as  $1\frac{1}{2}$  times the weight of the calcium-hydrate. With very good work, 166 parts of strong bleach can be obtained from 100  $\text{Ca}(\text{OH})_2$ . The amount of  $\text{MnO}_2$  required for making 100 parts of bleach, testing 36 p.c. in the chamber, is by theory, 44 parts, *i.e.*, 63 parts of 70 p.c. ore. Practically never less than 75, and on an average 90 parts of 70 p.c. ore is consumed, principally owing to the incomplete utilisation of the ore.

The quantity of hydrochloric acid varies even more with the method employed. 100 parts of 36 p.c. bleach contain as much chlorine as 37 parts dry  $\text{HCl}$  = 116 acid of  $32^\circ \text{Tw.}$ , or the quantity obtainable from 65 parts of common salt (testing 92 p.c.  $\text{NaCl}$ ). When working with (native or recovered)  $\text{MnO}_2$ , even theory requires doubling those quantities, as  $\text{MnCl}_2$  must be formed; the Deacon process and others *theoretically* utilise all the chlorine of  $\text{NaCl}$ ; but in all cases practically a large excess of acid has to be employed. In ordinary practice 1 ton of 36 p.c. bleach can be made by the old process from 4 tons of salt, but in France, working very carefully with small stills, very much better results are stated to be attained—namely, 1 ton of bleach from 3 tons of acid of  $36^\circ \text{Tw.}$

The results obtainable with the Weldon and Deacon processes have been stated in another place.

Bleaching powder must be packed in very well-made casks, preferably made of hard wood, and lined with strong brown paper, both round the sides and at the ends. The latter are sometimes secured by a coat of plaster of Paris. This is done in order to prevent the access of air, which quickly deteriorates the powder both by its moisture and its carbonic acid. J. C. Steele (E. P. 3,902, 1881) recommends packing it in boxes made of shavings, paper, or paste-board, pasted up and then well soaked in melted wax or paraffin (of course only for retail purposes).

The packages must be kept in cool, dry places; both rain and sun would quickly spoil the bleaching powder, even if packed in good casks.

*Properties of bleaching powder.*—Good bleaching powder is a pure white powder, often mixed with lumps which, however, ought to be

transformed to the core, and which are often removed by riddling. It has a peculiar smell, quite different from that of chlorine, and not owing to hypochlorous acid, since it is just as perceptible in alkaline solutions, or on the skin after washing with soap, &c. It may possibly be due to the action of the compound upon organic matter.

In the air bleaching powder attracts moisture and carbonic acid, and gradually changes into a pasty mass. Mixed with a little water, it forms a stiff paste, with a perceptible swelling and rise of temperature; this is probably caused by the transformation of  $2\text{CaOCl}_2$  into  $\text{Ca}(\text{OCl})_2$  and  $\text{CaCl}_2$ .

Bleaching powder decomposes gradually even in closely stoppered bottles or well protected casks. The presence of light, heat, moisture, and carbonic acid greatly accelerates this change; so does shaking, *e.g.* in transit. Hence the strength of bleach is usually only guaranteed at the place of shipment, but it ought not to lose above 2 or at most 3 p.c. by a few weeks' journey.

Experiments on the rate at which bleaching powder loses its available chlorine have been made by J. Pattinson in 1874 (C. N. 29, 143), and 1886 (S. C. I. 1886, 587). He experimented in the first case with samples kept in loosely corked bottles, sheltered from direct sunlight, and found that these lost on an average 0.33 p.c. monthly from February to April, 0.86 from June to September, 0.28 from November to January. The greatest loss occurred in August, *viz.*, 1.4 p.c. per month. In the course of twelve months the strength of 28.7 p.c. bleach came down to 20.8; that of 37.6 p.c. to 28.2 or sometimes not lower than 32.3 p.c. thus showing that weak bleach, contrary to the formerly general assumption, is no more stable than strong.

On the second occasion he examined the bleach by storing it both in casks (marked A, B, and C) and in bottles, both of them kept in a cellar where the variations of temperature only ranged from  $5^\circ$  to  $17^\circ \text{C.}$  (of course, as he points out, in practice the bleach will mostly have to be stored in places where the temperature in summer reaches  $21$ – $27^\circ \text{C.}$ , so that the loss of chlorine will be greater than in his experiments). The change produced by keeping for twelve months (detailed statements are given for each month in the original) was as follows (in per cent.):—

Original available Chlorine	Loss of available Chlorine		Loss of total Chlorine		Material serving for manufacture
	Casks	Bottles	Casks	Bottles	
A. 37.00	3.20	2.30	1.36	0.86	Irish limestone
B. 38.30	3.20	1.80	1.45	0.43	ditto
C. 36.00	3.10	1.80	1.71	0.68	French cliff

If, however, it is taken into account that the bleach in the casks absorbed carbonic acid and water from the atmosphere during the year, and thereby increased in weight, it is found that the loss both of available and total chlorine is but slightly greater in casks than in bottles.

The small quantity of chlorate originally present (about  $\frac{1}{2}$  p.c.) was found to have vanished completely after four months. Some  $\text{HOCl}$  must hence have been driven out by  $\text{CO}_2$ , and a little more  $\text{CaOCl}_2$  (as well as the chlorate) must have given up oxygen in order to form  $\text{CaCl}_2$ .



The experiments made by Lunge and Lando (J. S. D. and C., 1885, Nov. 25), with bleach-liquor have also shown that the action of the air is nothing like so injurious to the stability of such solutions as that of the light, which ought to be excluded by all means. Solutions kept in the dark, in closed vessels, remained practically unchanged up to the twenty-fourth day, and up to the thirty-third day, when the experiment was finished, the strength had only decreased from 29.58 to 29.12 p.e. Kept in open vessels in the dark, they remained unaltered up to the twelfth day; on the thirty-third day they had lost 3.30 p.e. But when kept in closed vessels in diffused daylight, the decomposition set in at once, and on

the thirty-third day only 8.52 p.e. remained of 33.02 p.e. originally present. Solutions of chloride of magnesium behaved similarly to those of chloride of lime; those of zinc or aluminium hypochlorite, as might be expected, were much less stable.

A few experiments made by Thümmel (Ar. P. 22, pt. 1 (1834)), also prove that light has much more action on bleaching powder than exposure to air.

The following complete analyses of the samples of bleaching powder investigated by J. Pattinson (*v. supra*) may serve as an example of the best descriptions of the commercial article:—

	A made of Irish limestone (from Larne)	B made of Irish limestone by another manufacturer	C made of French cliff
Available chlorine . . .	37.00	38.30	36.00
Chlorine as chloride . . .	0.35	0.59	0.32
Chlorine as chlorate . . .	0.25	0.08	0.26
Lime . . . . .	44.49	43.34	44.66
Magnesia . . . . .	0.10	0.31	0.13
Peroxide of iron . . . . .	0.05	0.04	0.02
Alumina . . . . .	0.13	0.11	0.33
Oxide of manganese . . .	trace	trace	trace
Carbonic acid . . . . .	0.18	0.30	0.18
Siliceous matter . . . . .	0.10	0.30	0.50
Water and loss . . . . .	16.15	16.33	17.00
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00
Total chlorine . . . . .	<hr/> 37.60	<hr/> 38.97	<hr/> 36.58

The following are the analyses of bleaching powder made in the author's laboratory, by Schäppi, from perfectly pure lime and with the greatest care, so as to obtain the strongest possible product:—

Available chlorine . . . .	43.13
Chlorine as chloride . . . .	0.29
Lime . . . . .	39.89
CO <sub>2</sub> . . . . .	0.12
H <sub>2</sub> O (direct estimation) . . .	17.00

Calculated as:

CaOCl <sub>2</sub> + H <sub>2</sub> O . . . . .	88.08
CaCO <sub>3</sub> . . . . .	0.96
CaCl <sub>2</sub> . . . . .	0.45
Ca(OH) <sub>2</sub> . . . . .	6.74
H <sub>2</sub> O not combined . . . . .	3.77

100.00

The small quantity of unchanged calcium hydrate is proof for the opinion that this is merely lime mechanically protected against the action

of chlorine by the bleaching compound CaOCl<sub>2</sub>, previously formed.

A. E. Fletcher, in a paper read before the British Association in 1887, gives the following figures for the production of bleaching powder in the United Kingdom, including chlorate of potash (taking 1 ton of this = 5 tons of bleaching powder, which is certainly too low, 7 or 8 tons being the real equivalent).

Year	Tons	Year	Tons
1877	105,529	1882	135,170
1878	105,044	1883	141,868
1879	115,290	1884	128,651
1880	131,606	1885	132,761
1881	135,826	1886	136,234

According to I. Levinstein (S. C. I. 1886, 356), the export of bleaching powder from England and its value were as follows:—

	1883	1884	1885
Exported quantity, tons . . .	80,030	80,030	75,107
Value . . . . .	£480,278	£661,406	£507,345
Market value per ton, from . .	£4 7 6	£9 10 0	£6 10 0
ditto to . . . . .	£9 10 0	£7 10 0	£6 5 0
ditto in 1886 . . . . .	£5 12 6	—	—

**Liquid chloride of lime or Bleach-liquor.** Formerly many bleachers used to make their chloride of lime by passing chlorine gas into or over milk of lime. This is now done at such

alkali works as are conveniently near bleach works, so that the cost of carriage of bleach-liquor is not considerable, and is more than counterbalanced by the gain of fully saturating

the lime, and especially that of saving the trouble and loss in dissolving the bleaching powder previous to using it.

On a laboratory scale the chlorine would be passed into the milk of lime. On the large scale this cannot be conveniently done, and is replaced by bringing the chlorine into contact with a continually renewed surface of the absorbent. This might be done in towers on the principle of acid-condensers, but there are some drawbacks to this, and the general plan is to employ cast-iron vessels provided with mechanical agitators so constructed that the liquid is not merely circulating round and round, but that its surface is continually renewed. In most cases these are cylinders standing on their base, with a vertical agitating shaft and horizontal arms; horizontal agitating gear is much more efficient, but is more troublesome, owing to the necessity of passing the axle through stuffing-boxes in the sides of the vessel. Even with the ordinary upright cylinders, the absorption of chlorine is quite complete, if three or more vessels are used in succession, so long as the agitator is at work, but the absorption ceases almost the moment the agitation ceases, from one cause or another.

In making bleach liquor, the agitators are charged with a milk containing about 1 to  $1\frac{1}{3}$  lbs. of slaked lime per gallon of water. The chlorine must not be evolved too fast, because this causes too great a rise of temperature. The rule is not to exceed  $32^{\circ}$ , or at most  $37^{\circ}$  C.; over this point the hypochlorite is very quickly changed into chlorate (comp. *Potassium chlorate*). It is very desirable that the absorbers should be surrounded by a cold-water jacket, to avoid that contingency. When the sp.gr. has risen to 1.040, the operation is stopped by turning the gas on to the next agitators; the first vessel, after the charge has been run off and it has been refilled with fresh milk of lime, will now be the last of the series.

Well-finished bleach liquor contains a very small quantity of free lime, generally with a slight excess of  $\text{CaCl}_2$  or of  $\text{Ca}(\text{ClO}_3)_2$ . The bulk of the chlorine is present as  $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2$ .

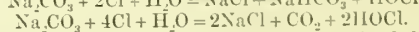
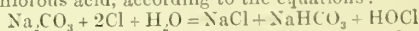
A much more active, but very quickly decomposing bleach liquor is obtained by employing, in lieu of  $\text{Ca}(\text{OH})_2$ , calcium carbonate, in which case free hypochlorous acid is formed.

$\text{CaCO}_3 + 4\text{Cl} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HOCl} + \text{CaCl}_2$ . Such liquor, to be made from the lime-mud obtained in causticising soda, has been patented by Deacon (1872). It is also produced in some processes for dealing with weak chlorine by Weldon and Solvay, in which case it is afterwards to furnish strong chlorine by decomposing it with acids; but this has never been practised on a working scale, and would be undoubtedly too expensive.

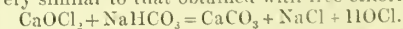
**Chloride of potash** (*Eau de Javel*). This liquor was first made in 1792 at the Javel works near Paris, and was the first bleaching compound known. It was then made by passing chlorine into a solution of potashes (crude potassium carbonate) in eight parts of water. This liquor is rarely made now, because it has been replaced by the cheaper compound made from soda, which has now mostly usurped its name.

**Chloride of soda** (*Eau de Labarraque*, usually called *Eau de Javel*; *Chlorozone*). This liquor

can be made by passing chlorine into a solution of sodium carbonate in 10 parts of water till the liquid begins to effervesce and bleaches litmus. In that case it contains more or less free hypochlorous acid, according to the equations:



Quite a different solution is obtained by adding to a solution of bleaching powder sodium carbonate or sulphate till no further precipitate is caused. The lime is then precipitated as  $\text{CaCO}_3$  or  $\text{CaSO}_4$ , and a mixed solution of  $\text{NaCl}$  and  $\text{NaOCl}$  remains. If in lieu of ordinary soda ash, bicarbonate is employed, the result will be very similar to that obtained with free chlorine:



The precipitate in this case settles better than with  $\text{Na}_2\text{CO}_3$ .

The liquors containing free  $\text{HOCl}$  have much more bleaching power than those containing sodium hypochlorite, but they keep very badly, the  $\text{HOCl}$  partly volatilising and partly losing its oxygen. Such a liquor is also obtained by passing  $\text{CO}_2$  into the ordinary neutral chloride of soda solution (Barnett and Slade's patent, 1872).

As an inodorous 'bleach-liquor,' C. A. Martin (D. J. 245, 46), proposes to add to a solution of bleaching powder portions of the following solutions—(1) 500 grams  $\text{KNO}_3$  in 10 litres of a  $5^{\circ}$  solution of aluminium sulphate; (2) 100 grams salicylic acid in 1 litre spirit; (3) 500 grams  $\text{KNO}_3$  and 500 grams  $\text{Na}_2\text{SO}_4$  in 5 litres water. The result is stated to be increased efficacy of the bleaching solution, together with the absence of the usual odour of chlorine-bleached goods.

The name 'chlorozone' has been given by Couët Dienheim-Brochocki to a number of preparations, patented in 1876 and subsequently down to 1885, produced by passing chlorine along with atmospheric air into a solution of caustic soda, either in such a way that all is converted into  $\text{NaCl} + \text{HOCl}$ , or that a mixture remains containing  $\text{NaOH}$ . Lunge and Landolt have shown<sup>1</sup> that the action of air is *nil*, and that the advantages claimed for chlorozone are quite illusory. This is fully confirmed by Storch.<sup>2</sup> It is very unlikely that the most recent patent of the inventor of chlorozone (G. P. 34,016), which involves the aid of electricity for 'ozoneing' the oxygen given off (by bad work) in the treatment with chlorine will lead to a different result.

*Bleach-liquors containing magnesia, zinc, or alumina*, all of them obtained by adding the sulphates of these bases to a solution of bleaching powder, are sometimes used for special purposes because they have a more rapid action than chloride of lime. Their properties have been fully investigated by Lunge and Landolt in the above mentioned memoir. They are never manufactured for sale, but prepared by the users themselves.

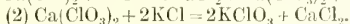
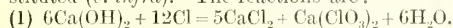
A very efficient bleach-liquor is prepared, according to L'Hermite, by the electrolysis of magnesium chloride. It is possible that this is only due to the formation of free  $\text{HOCl}$ , but

<sup>1</sup> Journ. Soc. Dyers and Colourists, Nov. 25, 1885.

<sup>2</sup> Ber. d. oesterr. chem. Gesellsch. 1885, p. 102; Fischer's Jahr. 1885, p. 256.

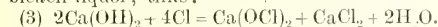
much more than that is claimed for the L'Hermite process by Bevan and Cross (S. C. I. 1887, 170; 1888, 292), whose conclusions have been very strongly contested by Hurter (*ib.* 1887, 337; 1888, 726 and 737). Comp. also Jurisch (C. J. 1888, 100). The whole subject, however, belongs more to the domain of bleaching than to the manufacture of chlorinic compounds.

**Potassium chlorate.** This salt is always manufactured by the process first indicated by Liebig: *i.e.* saturating milk of lime with chlorine under such conditions that calcium chlorate is formed, and afterwards decomposed by potassium chloride. For lime sometimes magnesia is substituted (*v. infra*). The reactions are:

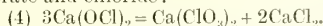


Hence only one-sixth part of the chlorine employed is, even by theory, converted into chlorate.

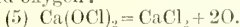
The first reaction is the formation of calcium hypochlorite and chloride, that is, ordinary bleach-liquor; thus:



Under certain conditions the calcium hypochlorite is subsequently changed into a mixture of chlorate and chloride:



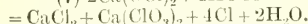
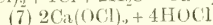
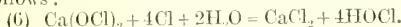
There is, however, a concurrent change, which must be avoided, as it involves a great loss, namely, the splitting up of hypochlorites into chloride and oxygen:



The conditions under which these changes occur, which were, of course, known in a general way before, have been exactly investigated by Lunge and Landolt (S. C. I. 1885, 722). They operated with a strong bleach-liquor, composed according to the above equation (3). When gradually heating this by itself for three hours up to 60°C. there was no perceptible change. Chlorate begins to be formed by equation (4), when heating another hour to 70°, more so when heating another two hours to 90°; but even after two hours' full boiling (altogether seven hours' heating), not much above  $\frac{1}{2}$  of the available chlorine originally present has been employed for the production of chlorate, according to equation (4). Oxygen begins to be given off from the first, and in the end the reaction (5) prevails over (4). Hence the conversion of hypochlorite into chlorate by mere heating is a very unfavourable process.

A second way of converting hypochlorite into chlorate consists in saturating the solution with chlorine. This even at 15° causes 70 p.c. of the  $\text{CaOCl}_2$  to pass into chlorate. On gradually heating the solution the reaction is quickened as soon as the temperature exceeds 40°, and it is complete at the boiling-point. Hence the presence of an excess of chlorine is a preventative against the reaction (5).

Most probably the excess of chlorine acts as follows:



That is, the free chlorine acts only as a carrier of oxygen from two molecules of calcium hypochlorite upon a third; the first two are reduced to chloride, the third is oxidised to chlorate, and

the free chlorine is fully regenerated in the end. The conclusions to be drawn for practice from Lunge and Landolt's experiments are as follows. The complete conversion of hypochlorite into chlorate is not effected either by mere heating or by a mere excess of chlorine, but both must act at the same time. A very large excess of chlorine is useless, perhaps even injurious. On the large scale the heat generated by the reaction suffices to complete the process. It is very injurious to allow the liquor to get heated unless there is an excess of chlorine present, because there is then a considerable loss of chlorate from the escape of oxygen.

Practically, chlorate of potash is manufactured in the following way.<sup>1</sup> Milk of lime is exposed to the action of chlorine in vessels provided with agitating gear, so that continually new surfaces are offered to the action of the gas which in this case is quickly absorbed, and completely so if the gas partially taken up in the first vessels is ultimately brought into contact with fresh lime contained in the last vessel. Formerly the absorbing vessels were made of stone, in an octagonal shape, and hence were called 'octagons,' which name is sometimes even now used for the cylindrical cast-iron vessels which have universally displaced the real stone octagons. Such cylinders (as shown in fig. 10) are, *e.g.* 10 feet wide and 5 feet 6 inches

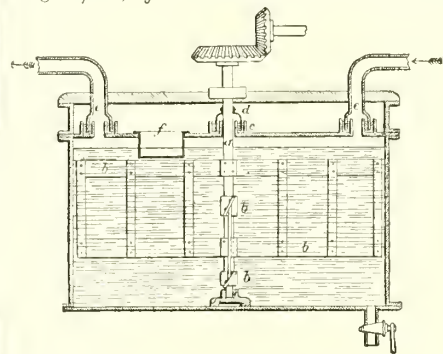


FIG. 10.

high, provided with a central vertical shaft *a* and agitating arms *b*, so contrived that they cause the liquid to well up and continually bring new portions of it to the surface. The shaft passes through an opening in the cover so constructed as to form a water-lute *c*, and a cup *d*, fastened on the shaft and dipping in the lute, prevents the escape of the gas round the shaft. Similar 6-inch lutes, *ee*, serve for introducing and taking away the gas. There is also a manhole *f*, fitted with an inner margin of strong sheet lead, reaching 6 or 7 inches downwards and forming a water-lute when the cylinder is filled. Apart from this the manhole is always open, so that observations can be made at any time, samples drawn and hydrate of lime put in. Sometimes a water jacket is applied outside. Three, or (better) more cylinders form a set working together, so that the fresh gas can be always turned upon that cylinder which is nearly

<sup>1</sup> According to Mr. E. K. Muspratt (S. C. I. 1886, 1087), this manufacture was commenced at St. Helens in 1847.



finished, whilst the cylinder charged with fresh lime receives the last gas. From the last cylinder there should be pipes leading to a small box charged with hydrate of lime, in case of any accident happening to the agitating machinery, when the absorption of chlorine in the cylinders would very soon cease. In lieu of this, a column charged with milk of lime can serve as well.

An excellent plan is the following, by which 10 tons of chlorate are made per week at a large works. There are five absorbing vessels, constructed as horizontally-placed semi-cylinders with raised sides, a horizontal agitating shaft passing through simple stuffing-boxes in the two plane ends. These vessels are made of cast-iron; they are surrounded by a water-jacket leaving a space of a few inches for cooling water. Two of these vessels (A and B), about 7½ feet long, 5 feet wide, and 6 feet high, are placed on the same level, the third, C, is placed a little higher, the fourth, D, and then the fifth, E, again a little more so. The fresh gas is passed into either A or B (one of them being cut off for emptying), then successively into C, D, and E. When A is finished the gas is turned into B, the contents of A are run off, those of B into A, C into B, D into C, E into D, and fresh milk of lime is put into E. All this is going on at the same time, the connecting taps being opened simultaneously. E is directly open to the air, and no smell whatever is perceptible there. The stuffing boxes, which are packed with hemp, must be pretty frequently renewed.

At Kuhlmann's works there is an absorbing apparatus, made of iron lined with lead, in which the gas is forced through the liquid, and is made to ascend in a spiral line by means of a spout turned bottom upwards, mechanical agitation being provided in the same sense. This apparatus produces excellent absorption, but wears out very quickly.

The milk of lime must be prepared in such a way that the finished liquor becomes of a certain strength, which is, however, not the same at all works. The specific gravity of the milk of lime itself should not exceed 16° or 17°Tw.; that of the finished liquor 28° to 32°Tw. Some manufactures go as far as 40°Tw.

The reaction causes an elevation of temperature which up to a certain extent is useful; but it must not be allowed to get too high, because in this case oxygen is evolved, and there is a corresponding loss of chlorate. In no case can the theoretical proportion of 1 chlorate to 5 chloride be attained; there is always some HCl carried on with the chlorine, and probably on the large scale the evolution of oxygen cannot be entirely avoided; but with good work the proportion can be kept at 1:5.5 or even 1:5.4.

Part of the lime can be replaced by weak bleaching powder which sometimes contains a good deal of chlorate; but this must not be heated before being saturated with chlorine, as otherwise much oxygen is lost (*cf. supra*). Some weak bleach contains much more  $\text{CaCl}_2$  than  $\text{CaClO}_2$ , and is not at all suited for this purpose.

As the reaction proceeds, froth appears on the surface and the liquid becomes warm. In the first agitator the temperature should be from 65 to 70 C.; if it gets hotter, water-cooling

is resorted to, or else the gas is cut off for a while. Afterwards the liquid turns pink, and the froth mostly vanishes again. The operation may be considered as finished when a sample taken out settles quickly and completely, leaving little sediment, smells of chlorine and bleaches litmus paper. On adding hydrochloric acid in the cold it should not give off chlorine (as hypochlorite would do). The pink colour is caused by calcium permanganate; it appears with Deacon bleach as well, since all lime contains sufficient manganese to produce the reaction. The operation lasts two or three days with strong chlorine, and twice as long with Deacon chlorine.

The contents of each agitating vessel, as they are finished, are run into settlers provided with drop-siphons, and thence into the concentrating pans. In the settlers their volume and strength is accurately noted, in order to calculate the quantity of potassium chloride (technically called 'muriate of potash') required. This is done either from the results of a laboratory test, or from the indications of the hydrometer which must be compared with the former at each single works, the conditions not being the same everywhere. The potassium chloride should be of the strongest kind (95 p.c.), and a small excess of it should be used. Some add it to the agitating vessels, under the (probably mistaken) idea that  $\text{KClO}_3$  decomposes less easily than  $\text{Ca(ClO}_3)_2$ . Usually it is only added in the concentrating pans.

The mud left in the settlers is, of course, washed or filter-pressed; the washings can be used for making fresh milk of lime.

The liquor as it runs away from the settlers still smells of chlorine. This is a nuisance, and it also acts upon the vessels, but the addition of a small quantity of a reducing agent like sodium thiosulphate, or even tank-waste, entirely destroys the free chlorine.

The boiling-down pans are usually made of either wrought or cast-iron, and are heated by direct fire. Some employ leaden pans, under the idea that these are less acted upon than iron; but the investigations made by Lunge (S. C. I. 1885, 4), have proved that lead is really much more acted upon and the loss of chlorate is the same as when working in iron. No difference was found in this respect between wrought and cast-iron. Since wrought-iron pans are not liable to crack and are more easily repaired when partly worn out, they would seem preferable.

The boiling down is sometimes continued up to 70°Tw. (measured hot), in which case the mother-liquors after crystallisation are not worth working up. Or else the first concentration is only carried to 50–55°Tw., and the mother-liquor is again boiled down to about 75°Tw. in winter or 80°Tw. in summer. The salts obtained by the second operation must be recrystallised twice before becoming marketable.

There is always a great deal of mud found in the pans, partly from incomplete settling &c., partly formed by the action of the liquor on the metal. This mud must be removed by settling or by a filtering-drum before running the liquor into the coolers.

The coolers for the first salts are generally made of iron, since in no case can a pure pro-

duct be obtained at this stage. They are best made like those used for soda-crystals, with a plug-hole for running off the mother-liquor. They ought to be numerous enough to permit of the liquor remaining in them 9 or 10 days in winter and 14 days in summer. Here the crude chlorate of potash crystallises in long acicular crystals, totally unlike the thin plates in which the same salt crystallises when pure, but in reality possessing exactly the same faces, only developed in different fashion. They are easily distinguishable from the large transparent prisms of hydrated calcium chloride which appear if the concentration has been too great. They must be broken up after draining, and the adhering mother-liquor washed off with a little water, always taking care not to lose any crystals in the process.

The mother-liquor is a nearly saturated solution of  $\text{CaCl}_2$ , with a little  $\text{KCl}$  and  $\text{NaCl}$ , and with about 30 grams of  $\text{KClO}_3$  per litre. With bad work much more chlorate is left in the liquor, none of which can be recovered. In the very best case 10–12 p.c. of all chlorate manufactured is lost through this cause, usually much more (25–30 p.c.). Usually it is not even attempted to recover the chlorine from these liquors by heating with hydrochloric acid—they are simply run to waste. But, with due care, the mother-liquors can be quite well worked for chlorine by taking care to run the hydrochloric acid *in pari passu* with the liquor; but the temperature in the still must never get up to  $60^\circ$ , otherwise explosions easily occur through the formation of hypochlorous anhydride.

The great loss of chlorate in the ordinary process has given rise to the process of Muspratt and Eschellmann, where magnesia is substituted for lime (Eng. Pat. Nos. 3,960, 5,183, and 5,186 of 1883; No. 1,900 of 1885). A detailed description of this process has been given by Higgins (S. C. I. 1887, 248). The magnesia is obtained by burning Greek magnesite at not too high a temperature; when overburnt it is useless for the absorption of chlorine. The  $\text{MgO}$  is very finely ground, suspended in water, and exposed to the action of chlorine in the ordinary octagons. The reaction is not so violent as with lime. The temperature of a finished octagon is usually  $43^\circ\text{C}$ ., and it never exceeds  $60^\circ\text{C}$ ., but this matters all the less as no hypochlorite is formed in this way, the reaction passing on at once to chlorate. In the finished liquor the proportion of chlorate to chloride is very near to the theoretical, viz. 1:5.1 or less; this constitutes an important advantage over the lime process, 7 p.c. less chloride being formed. No pink colour appears with very pure magnesia, but it does when it contains manganese. The strength of this liquor varies from 1.20 to 1.25.

The octagon liquor is now boiled down to  $75^\circ\text{--}80^\circ\text{Tw}$ ., when on cooling about 50 p.c. of the chloride will crystallise out as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . The mother-liquor contains 1 mol. chlorate to 2.8 chloride. Potassium chloride is now added to it in as nearly as possible the theoretical quantity, and the potassium chlorate crystallised out. The mother liquors being much less in quantity than with lime, and  $\text{KClO}_3$  being less soluble in  $\text{MgCl}_2$  than in  $\text{CaCl}_2$ , the magnesia mother-liquors contain much less chlorate than

lime liquor (on an average 19 grams, down to 10 grams per litre), and the yield of  $\text{KClO}_3$  rises to 90 p.c. of the total.

The mother-liquor is treated with  $\text{HCl}$  to destroy the chlorate at a temperature not exceeding  $60^\circ$ , with due precautions against explosions. The still-liquor is now neutralised with  $\text{MgO}$ ; there is then a solution of kieserite ( $\text{MgSO}_4$ ) run in to decompose the calcium chloride present, and the gypsum, along with iron oxide, is settled out. The liquor is now concentrated in cast-iron pots (wrought-iron is acted upon too much); the iron dissolving in the liquor is oxidised to the ferric state, and is precipitated by  $\text{MgO}$ ; the settled liquor is run into barrels where it sets to a hard mass containing 47 p.c. of  $\text{MgCl}_2$ . This magnesium chloride is sold to cotton sizers.

This process would, of course, only become general if the magnesium chloride obtained as a by-product could be profitably decomposed for chlorine, as it is not saleable by itself in very large quantities, and could not compete in price with the Stassfurt article.

Such utilisation for the manufacture of chlorine had been intended by Weldon, who first proposed magnesia for the above purpose, and it is again mentioned in a patent of J. Wilson (No. 5,975, 1884). Twynam (No. 4,397, 1881) proposes dolomite, under the idea that double chloride of potassium and magnesium (carnallite) will crystallise out of the mother-liquor after the chlorate. (This seems quite hopeless, since the principal question is not that of saving  $\text{KCl}$ , but  $\text{KClO}_3$ .)

Another process for greatly reducing the loss of chlorate in the mother-liquors is that of Péchiney (*cf.* Weldon, S. C. I. 1882, 41, to which paper the author has added his own observations). He concentrates ordinary chlorate liquor made from lime of a density of  $25^\circ\text{Baumé}$ , up to  $48^\circ\text{B}$ . (hot), and cools it down to at least  $12^\circ\text{C}$ ., but not below  $10^\circ\text{C}$ . Of its 5.5 mol. of  $\text{CaCl}_2$ , 4.3 are thus caused to crystallise out as  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (probably it should be  $6\text{H}_2\text{O}$ ), but if the temperature were allowed to fall below  $10^\circ$ , calcium chlorate would crystallise as well. The crystals are separated by a hydro-extractor, and the mother-liquor is now converted into potassium chlorate by addition of  $\text{KCl}$ ; there being only 1.2  $\text{CaCl}_2$  present to 1  $\text{KClO}_3$ , the mother-liquors cause a very much smaller loss than in the ordinary process. Péchiney's process is specially suited, and was originally invented, for the manufacture of sodium chlorate (*cf. infra*). It is evidently only possible to work it in the cold season.

The crude chlorate of potash is always purified by recrystallisation ('finished'). For this purpose it is redissolved in a mixture of water and of the mother-liquor obtained in the finishing process, which is done in a lead-lined vessel, with the aid of steam, preferably indirect (dry) steam. The solution is made at a full boiling heat, sometimes with the addition of very small quantity of sodium carbonate and of sodium sulphide, in order to precipitate any iron and lead present as chlorides; it is made up to  $25^\circ\text{Tw}$ .,

<sup>1</sup> The intermediate formation of a calcium oxychloride described in Péchiney's patents and Weldon's paper has since been given up.

and, after good settling and straining through canvas, the liquor is run into the coolers. These are always made of wood lined with lead; they are either of a deep pattern, with wooden laths placed inside for the crystals to adhere to, or else they are made quite shallow, but covered over to prevent any too rapid cooling. The crystallisation lasts from 8 to 14 days, according to the season.

The crystals are drained, preferably by means of a hydro-extractor, in which the last operation, the washing, can be also effected with great ease and completeness. This is imperative, since it is required that chlorate of potash should show little or no trace of chlorides; 0.05 p.c. being a maximum sometimes stipulated. So long as there is  $\text{PbCl}_2$  present, this cannot be very easily effected, but the lead can be removed in dissolving, as stated before. The mother-liquors and washings are used over again till they become too impure, when they go back to the boiling-down pans. The crystals are dried on a hollow iron plate, covered with sheet lead and heated by steam.

Chlorate of potash is either sold as 'crystals' or 'ground.' For the former purpose the crystals, as they come from the drying plates, are sifted through a sieve with eight holes to the linear inch, or less, as the case may be. The powder is best ground while still slightly warm. The mills may be of any description, horizontal, edge runners, rollers; but the chlorate during grinding ought not to come into contact with iron, nor with any organic substances (straw, wood chips, &c.), or dangerous explosions may occur. It must be sifted through a revolving sieve, made of miller's gauze, with mechanical brushes. The powder ought to be snow-white and without any grittiness, like fine flour. The crystals ought to be in thin, large, brilliant transparent plates; excessive drying will make them opaque. Both are usually packed in 1 cwt. kegs, laid out with blue paper.

Formerly it was generally assumed that 1 part of chlorate of potash required 7 or 8 times as much chlorine as 1 part of bleaching powder, but with the new processes the yield is, of course, better than that. There is, however, even now a manufacturing loss of about 30 p.c., or at least 25 p.c. One ton of chlorate in the ordinary process requires about thirty tons of hydrochloric acid of 30° Tw.; if the mother-liquors are utilised for producing chlorine without this, forty tons of acid will be used. This refers to Weldon chlorine; by combining the Deacon and Weldon process, and utilising the mother-liquors as before, the consumption of acid ought not to exceed 22 tons. One ton of chlorate requires, moreover, 17-18 cwt. of 90 to 95 p.c. muriate of potash,  $2\frac{1}{2}$  to 3 tons of lime, and 15 or 16 tons of coal. The wages are but insignificant in proportion to the value of the article.

Chlorate of potash is principally employed for the manufacture of lucifer matches, for pyrotechnical purposes, for fuses, for some description of gunpowder, and other cases where it is a constituent of explosive materials. It is also largely employed, on account of its oxidising properties, in dyeing and calico-printing, in the manufacture of alizarin, &c. Moreover, it is

used in laboratories for preparing oxygen, and in medicine, especially for gargling. The quantity manufactured in the United Kingdom in 1887 is estimated at 7,000 tons. Somewhat considerable quantities are also made in France, Germany, and Austria.

**Sodium chlorate.** This compound, which formerly was only a chemical curiosity, has become of technical importance, since it was found that it is much more suitable for the preparation of aniline black than potassium chlorate, owing to its greater solubility.

At first when a demand for it sprang up, it was made from potassium chlorate by means of hydrofluosilicic acid (*cf.* Lunge's *Alkali*, 3, 320), and was sold at two or three times the price of the potassium salt. It was at that time thought that it could not be prepared from the calcium-chlorate liquor of the ordinary process, just because  $\text{NaClO}_3$  is very soluble, and cannot be separated from  $\text{CaCl}_2$  by crystallisation. But this difficulty can be avoided, as we shall see.

The process of Bottomley and Molesworth (*Pat. No. 3,005, 1881*) consists in treating a hot saturated solution of potassium chlorate with one of bitartrate of soda, and separating the precipitated potassium bitartrate from the solution of sodium chlorate. This was also to be done with the ordinary calcium chlorate liquor; in which case, of course, calcium tartrate would have been obtained. Since some loss of tartaric acid could not possibly be avoided, this process would be even more expensive than the first mentioned.

The real manufacture of chlorate of soda by a cheap process was first carried out by Pechiney, by means of his above-mentioned process of removing most of the calcium chloride from the crude liquor by crystallisation. The purified liquor, thus accumulated during the colder part of the year, is mixed with a solution of ordinary sodium sulphate, previously neutralised by lime. The operation is carried out in this way. An excess of solution of  $\text{Na}_2\text{SO}_4$  is added to the chlorate liquor with continuous agitation; then more chlorate liquor is gradually run in, till the  $\text{Na}_2\text{SO}_4$  has been completely converted into  $\text{CaSO}_4$ . This condition, as well as that of a certain temperature, must be strictly observed in order to obtain the calcium sulphate in a crystalline form. The mixture is run into a tank containing a canvas-covered false bottom, and it is filled up to this with liquor from the last operation. After filling the remainder of the tank, the whole is allowed to stand for a few hours, after which the liquor is run off, but not below the filtering canvas. This process prevents the gypsum from passing through the filter; it is then put into a hydro-extractor, and in this is completely freed from sodium chlorate, with the help of washing by water. The solution of sodium chlorate is now concentrated by evaporation, during which most of the sodium chloride separates in the solid form and is fished out. The remaining solution on cooling yields crystals of sodium chlorate which are purified by recrystallising and washing the second crystals. The mother liquor always goes back into the process. The purified salt contains no more than 0.16 p.c.  $\text{NaCl}$ . Nearly all the chlorate contained in the liquor is really obtained by this



process, instead of the unavoidable loss occurring with chlorate of potash.

Chlorate of soda is also manufactured by Messrs. Muspratt by means of their magnesium chlorate liquor, freed from nearly half the  $MgCl_2$  by evaporation and crystallisation (*cf. supra*). To this liquor sodium carbonate or hydrate is added, till all the magnesia is precipitated as  $MgCO_3$  or  $Mg(OH)_2$ , in order to be used over again in the process. The remaining solution of  $NaClO_3$  and  $NaCl$  is concentrated by evaporation, with fishing out the  $NaCl$ , and after attaining  $100^\circ$  and  $106^\circ$  Tw. is allowed to cool down; the sodium chlorate crystallises out and is purified in the usual manner.<sup>1</sup> G. L.

**Hydrochloric acid.** Commercial hydrochloric acid is a more or less pure solution of hydrogen chloride  $HCl$  in water.

**Hydrogen chloride** is a colourless gas, of sp.gr. 1.2596 (air=1), and molecular weight 36.457. By weight it consists of 2.74 parts of hydrogen and 97.26 parts of chlorine. It can be condensed into a liquid by cold and pressure; the tension of this liquid is 26.2 atmospheres at  $0^\circ$  and 40 atmospheres at  $12.5^\circ C$ .

The heat of formation of a gram molecule of  $HCl$  is 22001 calories.

Hydrogen chloride has a great affinity for water and is greedily absorbed by it. The solution is the ordinary hydrochloric acid which, when somewhat concentrated, emits fumes of  $HCl$  on exposure to the air. The following table by H. Deicke shows the maximum solubility of  $HCl$  in water at varying temperatures.

1 cub. cent. dissolves at the temperature  $t^\circ$  :

$t^\circ$	Vol., $HCl$ at $0^\circ$ and 760 mm. dissolved in 1 vol. $H_2O$	Specific gravity of the saturated solution	Percentage of $HCl$ by weight in the solution
$0^\circ C$ .	525.2	1.2257	45.118
4	494.7	1.2265	44.361
8	480.3	1.2185	43.828
12	471.3	1.2148	43.277
14	462.4	1.2074	42.829
18	451.2	1.2064	42.314
23	435.0	1.2014	41.536

The behaviour of aqueous solutions of  $HCl$  under varying conditions of temperature and pressure has been principally studied by Roscoe and Dittmar (Q. C. J. 12, 128). We shall mention here only the fact that concentrated hydrochloric acid on heating loses both gas and water and gradually becomes weaker, until a sp.gr. of 1.101 and a percentage of 20.24  $HCl$  is attained at a boiling temperature of  $110^\circ C$ .; the acid in this state distils without change, provided the atmospheric pressure is 760 mm. At a lower pressure the acid distilling unchanged is stronger, at a higher pressure it is weaker. A similar, but not identical limit is attained when strong acid is exposed to the air at ordinary temperatures.

<sup>1</sup> Since the above article was written, a very exhaustive treatise on the manufacture of chlorate of potash has been published in German by Dr. W. Jurisch: *Die Fabrikation von chlorsaurem Kali* (Berlin, 1888). A few notes from this book are incorporated in the text of this article.

The following table gives the percentages of  $HCl$  in aqueous hydrochloric acid at various specific gravities and at a temperature of  $15^\circ C$ .:

Deg. Twaddell	Spec. gravity	Percentage of $HCl$	Grammes $HCl$ per litre	1 cubic foot weighs lbs.	1 cubic foot contains lbs. of $HCl$
1	1.005	1.12	11.32	62.66	0.70
2	1.010	2.12	21.45	62.97	1.34
3	1.015	3.12	31.67	63.29	1.97
4	1.020	4.11	41.99	63.60	2.61
5	1.025	5.11	52.11	63.91	3.26
6	1.030	6.11	62.93	64.22	3.92
7	1.035	7.10	73.55	64.53	4.58
8	1.040	8.10	84.27	64.84	5.25
9	1.045	9.10	95.09	65.16	5.93
10	1.050	10.09	106.01	65.47	6.61
11	1.055	11.09	117.02	65.48	7.31
12	1.060	12.09	128.14	66.09	8.00
13	1.065	13.08	139.36	66.40	8.69
14	1.070	14.08	150.68	66.71	9.40
15	1.075	15.08	162.10	67.03	10.11
16	1.080	16.07	173.62	67.34	10.83
17	1.085	17.07	185.24	67.65	11.55
18	1.090	18.07	196.96	67.96	12.28
19	1.095	19.07	208.78	68.27	13.02
20	1.100	20.06	220.70	68.59	13.76
21	1.105	21.06	232.68	68.90	14.51
22	1.110	22.06	244.80	69.21	15.27
23	1.115	23.05	257.02	69.52	16.04
24	1.120	24.05	269.34	69.83	16.79
25	1.125	25.05	281.76	70.14	17.57
26	1.130	26.04	294.28	70.46	18.35
27	1.135	27.04	306.90	70.77	19.14
28	1.140	28.04	319.62	71.08	19.93
29	1.145	29.03	332.44	71.39	20.73
30	1.150	30.03	345.36	71.70	20.54
31	1.155	31.03	358.34	72.02	22.54
32	1.160	32.02	371.44	72.33	23.16
33	1.165	33.02	384.64	72.61	23.99
34	1.170	34.02	397.94	72.95	24.82
35	1.175	35.01	411.34	73.26	25.65
36	1.180	36.01	424.84	73.57	26.49
37	1.185	37.01	438.44	73.89	27.34
38	1.190	38.01	452.14	74.20	28.20
39	1.195	39.00	466.00	74.51	29.06
40	1.200	40.00	479.84	74.82	30.00

#### THE MANUFACTURE OF HYDROCHLORIC ACID.

Before the ammoniacal soda process had revolutionised the economical conditions of alkali-making, hydrochloric acid ('muriatic acid' or 'spirits of salts') was manufactured by two entirely different modes. Nearly all of it was made as a by-product in the manufacture of sulphate of soda for the Leblanc process, in some cases only because the law compelled it to be condensed. A very large portion of this acid was obtained in too weak a state for sale or for most uses, and very much of it was actually run to waste. Most of it was used up immediately at the same works, principally for the production of chlorine, and only comparatively little found its way into the general trade. This state of matters brought about a close local connection between alkali works and all those industries consuming a large quantity of hydro-

chloric acid, the latter being accounted of very little value.

There remained, however, a certain number

$0^\circ$	$5^\circ$	$10^\circ$	$15^\circ$	$20^\circ$	$25^\circ$	$30^\circ$	$35^\circ$	$40^\circ$	$45^\circ$	$50^\circ$	$55^\circ$	$60^\circ$	$65^\circ$	$70^\circ$	$75^\circ$	$80^\circ$	$85^\circ$	$90^\circ$	$95^\circ$	$100^\circ$
1.168	1.165	1.163	1.160	1.157	1.154	1.152	1.149	1.147	1.144	1.142	1.140	1.138	1.136	1.133	1.131	1.129	1.127	1.125	1.123	1.121
1.158	1.155	1.153	1.150	1.147	1.145	1.142	1.139	1.137	1.134	1.132	1.130	1.128	1.126	1.123	1.121	1.119	1.116	1.114	1.112	1.110
1.148	1.145	1.143	1.140	1.137	1.134	1.132	1.129	1.127	1.125	1.123	1.120	1.118	1.116	1.113	1.111	1.108	1.106	1.104	1.102	1.099
1.138	1.135	1.133	1.130	1.127	1.125	1.122	1.119	1.117	1.114	1.112	1.109	1.107	1.104	1.102	1.100	1.097	1.095	1.093	1.090	1.088
1.128	1.125	1.123	1.120	1.117	1.115	1.112	1.110	1.108	1.106	1.103	1.101	1.099	1.096	1.094	1.091	1.089	1.086	1.084	1.081	1.079
1.118	1.115	1.113	1.110	1.107	1.105	1.103	1.101	1.099	1.097	1.094	1.093	1.090	1.088	1.085	1.083	1.080	1.078	1.075	1.073	1.070
1.108	1.105	1.103	1.100	1.097	1.095	1.092	1.090	1.088	1.086	1.084	1.082	1.080	1.078	1.075	1.073	1.071	1.069	1.066	1.064	1.061
1.098	1.095	1.093	1.090	1.087	1.085	1.082	1.080	1.077	1.075	1.073	1.071	1.069	1.067	1.065	1.063	1.061	1.059	1.057	1.055	1.053
1.088	1.085	1.083	1.080	1.077	1.075	1.073	1.070	1.068	1.066	1.064	1.062	1.060	1.058	1.056	1.054	1.053	1.051	1.049	1.047	1.045
1.078	1.075	1.073	1.070	1.067	1.066	1.063	1.061	1.059	1.057	1.055	1.053	1.051	1.049	1.048	1.046	1.044	1.043	1.041	1.039	1.037
1.068	1.065	1.063	1.060	1.057	1.055	1.053	1.050	1.048	1.046	1.044	1.042	1.040	1.038	1.036	1.034	1.033	1.031	1.029	1.027	1.025
1.058	1.055	1.053	1.050	1.047	1.045	1.043	1.040	1.038	1.035	1.033	1.031	1.029	1.027	1.025	1.023	1.021	1.019	1.017	1.015	1.013
1.048	1.045	1.043	1.040	1.037	1.035	1.032	1.030	1.027	1.025	1.022	1.020	1.018	1.016	1.014	1.011	1.009	1.007	1.005	1.003	1.001
1.038	1.035	1.033	1.030	1.027	1.024	1.022	1.019	1.017	1.014	1.012	1.010	1.008	1.005	1.003	1.001	0.999	0.997	0.995	0.993	0.991
1.028	1.025	1.023	1.020	1.017	1.014	1.012	1.009	1.007	1.004	1.002	1.000	0.998	0.995	0.993	0.991	0.989	0.987	0.985	0.983	0.981
1.018	1.015	1.013	1.010	1.007	1.004	1.002	0.999	0.997	0.994	0.992	0.990	0.988	0.985	0.983	0.981	0.979	0.977	0.975	0.973	0.971

of uses of hydrochloric acid which could not be thus localised, and since the carriage of this substance is both troublesome and expensive, it was found economical to manufacture hydrochloric acid on those spots where there was a somewhat large consumption, under such circumstances that it formed the principal product; namely, by decomposing common salt with sulphuric acid in cast-iron cylinders exactly similar to those used in the manufacture of nitric acid, employing such an excess of salt that the more costly ingredient, sulphuric acid, was fully utilised and a good yield of strong hydrochloric acid was obtained. The residual product, a mixture of sodium sulphate with 20 or 30 p.c. of common salt, was sold by the name of 'cylinder-cake' to glass-works at a very low price, and was frequently hardly saleable at all. This circumstance, connected with the great expense of labour, coals, and repairs, has made the cylinder process of manufacturing hydrochloric acid unremunerative for some time past.

During the last few years all the conditions of alkali-manufacturing have changed, and the hydrochloric acid must now be considered as a, or even as *the*, principal product of Leblanc alkali works. None of the latter can now exist without fully utilising its hydrochloric acid in one way or another, and undoubtedly most of the Leblanc works would have to stop if their expenses were not principally paid by the hydrochloric acid, whose value has considerably risen at the same time that that of soda ash has declined. This fact has naturally caused constant endeavours to be made to produce hydrochloric acid, or directly chlorine, from the waste liquors of the ammonia-soda works and from other materials hitherto neglected as worthless. In so far as these endeavours refer to the direct production of *chlorine* they are described in that article; those referring to the production of ordinary hydrochloric acid will be mentioned at the close of the present article.

*Hydrochloric acid obtained in manufacturing sodium sulphate (salt-cake).* When salt was first decomposed in order to obtain sodium sulphate for the Leblanc process, the hydrochloric acid evolved during this process possessed no value and was simply allowed to escape into the air. This continued to be the case even after that manufacture had attained a comparatively large extension, but the damage caused to the neighbourhood by the acid gases soon brought about the intervention of local authorities and courts of law, and manufacturers were compelled to seek means for condensing the acid. This was first successfully done by Gossage's coke-towers in 1836, but in the great majority of works there was still a considerable loss of acid gases, as was proved by a Belgian Parliamentary Commission in 1856. But it is decidedly owing to Lord Derby's Alkali Act of 1863 (which has been followed by several other Acts) that British alkali-makers were compelled, ultimately for their own good, to adopt thoroughly efficient means for condensing their hydrochloric acid, and this has benefited all other manufacturing countries as well.

In fact the reports made by the inspectors under the Alkali Acts form an invaluable record

of all the various steps taken for improving the condensation of hydrochloric acid, and these reports have contributed towards the spreading of a better knowledge of that process and to cause manufacturers to improve it up to the highest standard of efficiency.

The Alkali Acts of 1863 made it incumbent upon those decomposing salt to allow no more than 5 p.e. of the hydrochloric acid to escape into the atmosphere. An additional Act of 1871 prescribed that no more than 0.2 grain of HCl might be present in a cubic foot of the gas escaping from the factory into the air. This corresponds to 0.454 gram HCl per cubic metre, or about three ten-millionths by volume. The latter clause applies to the chimney gases as well, and not merely to those escaping directly from the condensing apparatus. Although this requirement was at first declared by many to be impossible of fulfilment, the actual results proved at once that it was quite possible, and the escapes registered by the Alkali Inspectors have averaged far below the limits assigned by the Acts. Thus, in 1885, the average escape of HCl in chimney gases has been 0.10 grain per cubic foot, or 2.39 p.e. Of the total amount produced in 1886, the figures have been respectively 0.10 grain and 2.13 p.e.

The principles to be followed in condensing hydrochloric acid are very simple, but, as is usual in such cases, much care is required in planning and working the apparatus for efficiently carrying them out to their fullest extent. There is, of course, only one way of condensing hydrogen chloride, namely, bringing it into contact with water, which is a most energetic absorbent for it, and thus forming ordinary hydrochloric acid, that is, a solution of HCl in water. But this extremely simple process is complicated by the fact that the hydrogen chloride evolved in the decomposition of common salt is always more or less, and sometimes to a very considerable extent, mixed with air or with the gases formed in the combustion of fuels; that this mixture itself is at a high temperature, and that an additional amount of heat is generated by the absorption of HCl in water. This makes it incumbent upon the manufacturer, (1) to bring the acid gases into the most extended possible contact with water, and (2) to cool them down to a limit compatible with good condensation.

According to a very ingenious theory of Th. Schloesing (patent of February 13, 1878) the condensation of HCl by water can be effected most completely and in a very small space indeed if the action takes place at a temperature above the boiling-point of the acid formed, but as this process, when tried in France, has yielded an acid not exceeding 25°Tw., it has been given up as unpractical. The hot dilute acid collecting at the bottom of the condenser is of too small a value.

The importance of thoroughly cooling the gases before and during the actual process of condensation was soon recognised in the practical working of the Alkali Act, and was universally acknowledged until quite recently, but it is contested now to some extent (*v. infra*).

The task of cooling the gases presents, of course, very different degrees of difficulty according to the way in which the decomposition of salt has been carried out. Where this has been done in iron cylinders, or in the ordinary

shallow iron decomposing-pans, the gases evolved are only moderately hot, and are, moreover, mixed with very little air, so that they can be easily cooled down to the required extent. The gases evolved from muffle-furnaces ('blind roasters'), from the Hargreaves apparatus and in other similar cases are already much hotter, and these require a more efficient plan of cooling. Hottest of all are the gases given off in 'open roasters,' in the Péchiney-Weldon process &c., and the cooling must be carried out accordingly.

The means employed for a preliminary cooling are the following:

1. Passing the gases through a long channel, outwardly cooled by air, consisting of pipes made of earthenware, glass, or cast-iron, or flues made of stones, bricks, &c.

2. Cooling the conducting-pipes &c. outwardly by a current of water.

3. Injecting into the gas a quantity of water sufficient to cool it to a certain extent by its own rise of temperature and evaporation, but not sufficient to condense more than a small portion, consisting chiefly of sulphuric acid carried away as an impurity, into the liquid form.

These processes are applied to the acid gases in very different manners, according to the heat they originally possess and the degree to which they are diluted with inert gases. The concentrated and but moderately hot gases from ordinary decomposing-pans are sufficiently cooled by conveying them through a certain length of earthenware pipes before they enter the condensers. Where the condensers are placed near the furnaces, the necessary length of piping is attained by taking the gases in a perpendicular row of pipes upwards and then downwards again. Sometimes as much as 250 or even 300 feet of piping is employed in this way, and the temperature can be thereby lowered from 170°C. down to 30° or 40°C. Such pipes are made in two different ways; either of fireclay or some other porous substance, in which case they must be boiled in coal-tar for 24 hours, in order to make them tight and at the same time resist the action of varying temperatures; or else they are made of stoneware which is by itself air-tight and acid-resisting. The latter description of pipes is much thinner, and is, therefore, better adapted for cooling the gases. Even glass pipes of about 12 inches diameter are usefully employed for this purpose, and have found very much favour, but they are of course more easily cracked than earthenware pipes, and should be protected against the action of rain and snow. These pipes are made slightly tapering, and are joined together by putting the thinner end of one into the thicker end of the next pipe. Sometimes a fine jet of water is allowed to enter at the hotter end, in which case very much of the acid is condensed already in the pipes. Such pipes are shown in fig. 11.

The hotter gas evolved from muffle furnaces (blind roasters) or the Hargreaves apparatus is generally first subjected to a preliminary cooling in flues made of bricks set in tar-mortar, or much better of acid-resisting stone. Such flues should not be carried underground, as in this case their cooling action is very slight and there



may be great escape of acid before it is recognised. They should be fully exposed to the sight, and at the same time to the cooling action of the air. Brick-flues are very liable to leak

through the joints; they act better if made of grooved bricks in a circular shape, as shown in fig. 12. In any case they must be kept tight by a good coating of tar.

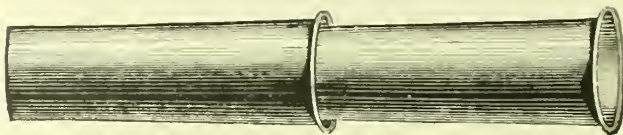


FIG. 11.

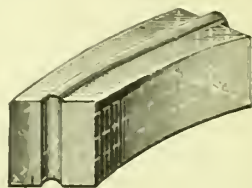


FIG. 12.

Stone flues are sometimes made in a circular shape, and these consist of two stones hollowed out to suit, as shown in fig. 13, or else they are made in the shape of shallow troughs, as shown in fig. 14. Such flues are specially adapted to the plan of running a small stream of water or weak acid along their bottom, which greatly promotes the condensation of acid.

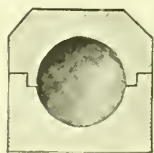


FIG. 13.

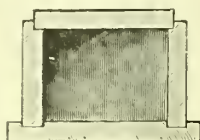


FIG. 14.

The hottest gases, as those evolved from open roasters, Mactear furnaces, and the like, may be first conveyed through a series of *cast-iron pipes*. Such pipes can be employed without any danger while the gases are hot, and they exercise a most excellent cooling action. But as soon as any acid can condense in them in a liquid form, they are at once acted upon and corroded. They must, therefore, be employed merely for a preliminary cooling, down to about 120 C., and the further conveyance of the gas must take place in stone or earthenware pipes. These iron pipes are usually cast in 9 feet lengths, 2 or 2½ feet wide, and 1 inch thick. As they have to be cleaned out now and then, they are best provided with plain ends, and are joined by means of a loose ferrule, cemented on both sides with tar and china-clay, which ferrule in case of need can be slipped sideways after softening the cement by heating, so that each length of pipe can be lifted out separately.

Of course the surface of the stone tanks, stoneware receivers, connecting pipes and condensers themselves, promotes a further cooling action, and, in order to aid in this the connecting pipes are frequently carried upwards and downwards to increase their cooling surface, as is seen in the apparatus shown further on, fig. 20. During the last years, there has been a tendency among the English alkali works to discard all preliminary cooling-pipes, and to leave all the necessary cooling to the action of the condensers themselves, which are made of such large size that they suffice for all purposes. It should be remembered that the heat brought along by the gases is often much less than that produced by the absorption of HCl by water in

the condensing-tower itself, which cannot of course be dealt with by any apparatus for preliminary cooling.

The cooling of the gases by the simple action of air is admittedly a somewhat uncertain proceeding, since it depends so much upon the temporary atmospheric conditions. In hot countries it is, of course, very slight in summer time. It is then sometimes supplemented by running a *stream of water* down the outside of the connecting-pipes, tanks, &c., or even by immersing the pipes completely in water. The latter plan is rather risky on account of leakage and cracking. Or else the gases are passed through a refrigerator, consisting of a stone tower, in the interior of which glass-tubes are arranged through which a stream of water is kept flowing. A very ingeniously constructed apparatus of this kind has been patented in connection with the Péciney-Weldon chlorine-process (*cf.* S. C. I. 1887, 784).

One of the most efficient plans for cooling the gases is to *bring them into contact with water itself*, whose evaporation absorbs a large quantity of heat. This can be regulated in such manner that either very little hydrochloric acid is condensed, and the resulting liquid consists principally of sulphuric acid, ferric chloride, and other impurities, or that a certain quantity of hydrochloric is condensed and employed directly, or for the purpose of feeding other condensing apparatus. To this class of cooling contrivances belongs the plan previously mentioned of running a little water along the bottom of the cooling pipes or flues. It is also carried out by injecting a spray of water, divided into a fine mist, into stone tanks, placed between the furnaces and condensing-towers (Newall and Bowman's Patent, June 15, 1874), and most frequently in the way shown in fig. 15. This figure represents a small tower, say 4 × 4 × 8 feet inside, made of stone flags in the usual manner. The hot acid gases enter near the bottom, below a stone grating on which there is a packing of earthenware dishes, or some equivalent contrivance for dividing the current of the gases and spreading the water, run in at the top, over the inside of the tower. The stream of water kept up here is only sufficient to keep the packing always in a moist state; much of it evaporates, and passes on with the gas from the top of the small tower, while a certain quantity of hot liquid collects at the bottom, and is found to consist almost entirely of the sulphuric acid carried away from the furnaces. Thus the gases are both cooled

and are to a great extent purified at the same time. On issuing from the tower, they are sometimes conveyed through a somewhat considerable length of piping, so that further cooling by the air takes place before they enter the condenser; if this string of pipes is carried in an ascending direction, the liquid condensing therein will always run back into the small tower, and by its evaporation increase its cooling action.

The *condensation proper* is always effected by bringing the acid gases into extended contact with surfaces of water which, by its great absorbing power for HCl, retains this gas in the

since by its aid the acid is obtained in the most concentrated state, and the outward cooling action on the surface of the vessels is also very favourable. But it is hardly possible to exhaust the acid gases in this way anything like completely, and the second description of condensing-plant ought therefore to be applied as well.

This consists in dividing the current of gases into a great many fine jets which are made to change their direction as often as possible, and bringing these into contact with water, spread out in very thin layers over a very large surface. Usually one and the same contrivance effects both the purpose of dividing the gaseous current and of spreading the feeding-water over a large contact surface. This has been first attained in Gossage's coke-towers, patented in 1836, which up to this day are employed in the great majority of alkali works. Recently other contrivances have been proposed as more efficient than coke-towers, and producing complex condensation in a much smaller space, but the general principle is the same.

The comparative efficiency of various modes of treating liquids with gases has been discussed theoretically by Hurter (S. C. I. 1885, 639, and 1887, 707).

In all the best condensing-plants both the just-mentioned kinds of apparatus are combined; first the bulk of the acid is condensed by means of the weak acid coming from the tower, and then the gases are completely deprived of hydrogen chloride by means of a coke tower or equivalent apparatus. Hence in a well-arranged plant no weak acid is produced at all as a final product.

We shall now describe the apparatus used for condensing hydrochloric acid according to the most approved principles, pointing out the various ways in which the end can be attained.

The apparatus must begin with the pipes or flues conveying the gases from the decomposing-pans and saltcake furnaces. As we have seen above, these must be of various kind according to the nature of the gases; their length, width, and material is influenced thereby. Where no 'cooling-tower' (*v. infra*) is employed, the extent of piping is generally greater than in the opposite case, say at least 100 feet for pan gas or 200 feet for roaster gas; but recently, as we have seen, this length has been diminished. Pan gas is conveyed in 12-inch pipes, made of glass, fireclay, or stoneware; roaster gas from muffle furnaces in flues made of brickwork or stone, to be followed by earthenware pipes of from 15 to 18 inches diameter; gas from open furnaces for a certain length in cast-iron pipes of 2 feet diameter, afterwards also in earthenware pipes.

Preferably, in lieu of such long pipes or flues, a shorter range is laid down, and the gases, while still hot, are passed through a *cooling-tower* of the kind described above, say 4 × 4 feet wide and 6 to 8 feet high inside, in which they are brought into contact with enough moisture to cool them down to a great extent, and to condense most of the sulphuric acid accompanying the hydrochloric acid. From here they are conveyed in a string of earthenware pipes, or in two parallel strings, to the stone cisterns or jars, where the strongest acid

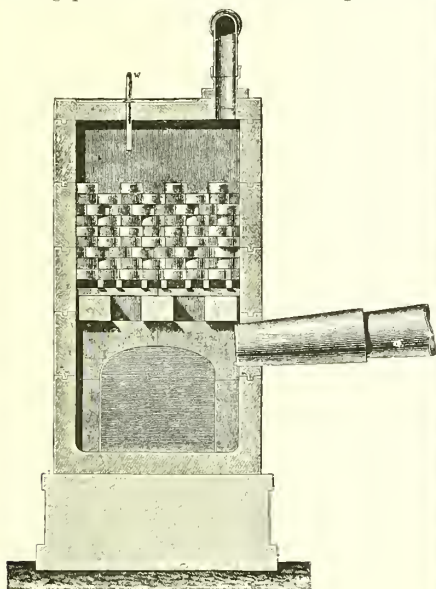


Fig. 15.

shape of liquid hydrochloric acid and ultimately washes it out of the gaseous mixture so that the escaping gas is almost absolutely free from HCl. This process is only then carried out in a rational manner, if it succeeds on the one hand in effecting a complete condensation of the acid, that is, a complete removal of the HCl from the gases, and if, on the other hand, it furnishes hydrochloric acid of sufficient strength for direct application or for sale.

The apparatus employed for condensing hydrochloric acid is principally of two different kinds. In the first kind the gases are made to travel in a large, undivided stream over a somewhat large quantity of water, whose great affinity for hydrogen chloride will attract this compound to such an extent that most of it is removed from the gases, provided the water surface is large enough and the apparatus is arranged in a rational manner, as will be described hereafter.

This process may be carried out in a few large stone cisterns, or in a considerable number of stoneware jars (receivers, Woulfe's bottles, bombomes, touries). It is very efficient in its way, and its application is very much to be recommended as the first stage of condensation,

is made. In England it is usual to employ for this purpose *stone tanks* or *cisterns*, say 5 × 7 feet wide and 3 or 4 feet high inside, of which

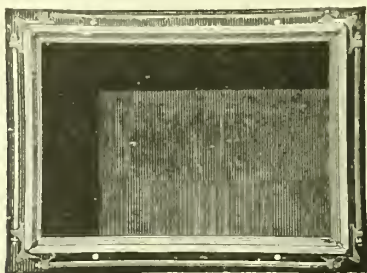


FIG. 16.

generally from three to six are combined. Such tanks are sometimes hollowed out of a single piece of stone, but this is in most places too

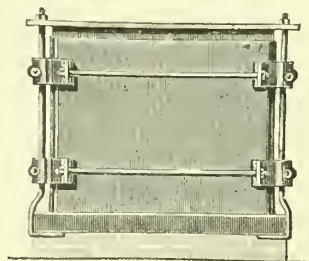


FIG. 17.

costly; they are, therefore, usually composed of single flags, 4 to 6 inches thick, held together either by 'bevel joints,' as shown in figs. 16 and 17, or by feather-and-tongue joints, as in fig. 18.

The flags are bound together by strong iron

ties, as shown in the diagrams; the joints are made tight either by thick india-rubber cord, laid between the faces of each two stones, or by a mixture of tar and fireclay ('black stuff'). The stones to be used for this purpose must be acid-proof, and able to resist heat. Some descriptions of stone can be used without any special preparation, as the silicious sandstones from Southowram in Yorkshire, or those from Herdecke in Westphalia, or the volvic lava from the Puy-de-Dôme; other stones, which are too porous, must be boiled in coal-tar for a week or so, after having been properly dressed by the stonemasons, before being put together. A set of such tanks is shown in fig. 19.

In France, Germany, and other countries large cisterns of this kind are sometimes used as well; but at the majority even of the large works *stoneware jars* (*receivers*), in the shape of large Woulffe's bottles (*bombonnes, touries*), are preferred, *aa*, as shown in fig. 20. Of these a long row, or sometimes two parallel rows, are combined in such manner that the acid gases pass onward from the furnace towards the final tower through the elbow pipes *cc*, and the liquid acid travels the opposite way, rising in each receiver from the bottom through the pipe *c*, and overflowing at *d* into the next receiver. Thus a continuous slow stream is established, and the surface of the liquid in *aa* is continuously renewed; and as the streams of acid and water flow in an opposite direction, they act upon each other in the most advantageous way; the strong acid arriving at those receivers which are nearest to the furnace is met there by the most concentrated gas, and can thus absorb still more HCl, in spite of the high temperature existing there, the HCl present in the atmosphere checking the volatilisation. On the other hand, the gases, when deprived of most of their HCl at the opposite end of the row, there meet with fresh water or very dilute acid, which absorbs HCl even from such weak gases. In only one place the set of

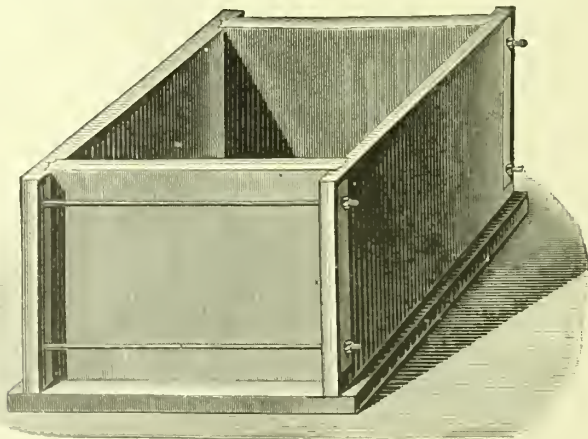


FIG. 18.

receivers is fed with liquor, namely, at the end farthest from the furnace, and equally, only in one place the finished acid runs off, namely, at the end nearest to the furnaces.

The size of each individual receiver varies from about 50 to 100 gallons, rarely much more or less. The number employed in a set varies from 40 to 100, but if the larger number is



employed, they are generally arranged in two parallel rows, which, after a certain time, when the greater part of the HCl has been absorbed, merge in a single row, as seen in the plan, fig. 21. The last of the receivers should be formerly left open to the air, or was connected with a chimney;

but it has been found much better to connect it with a coke-tower or similar apparatus, for a reason to be explained just now.

These stoneware jars are sometimes cooled from the outside by a stream of water; but this causes them to crack more easily than is other-

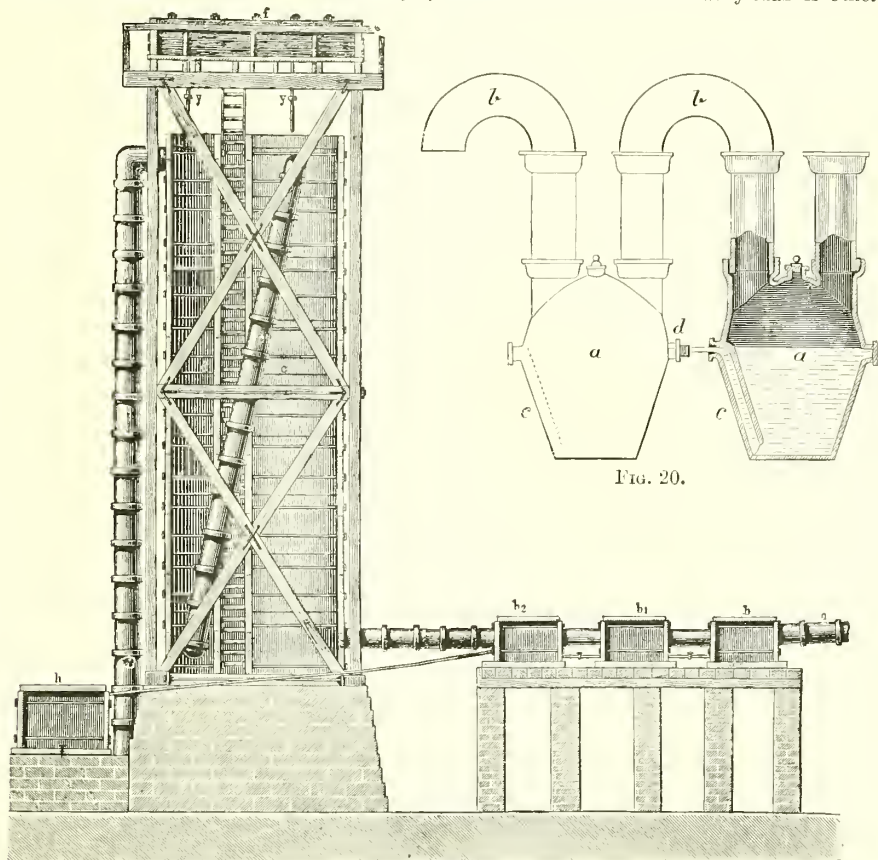


FIG. 19.

wise the case, and it is usually omitted. But it is very useful to aid the air-cooling by making the connecting elbows very high, as shown in fig. 20. These jars should be of the very best stoneware, which is able to resist somewhat violent changes of temperature. Fig. 21 shows a whole set of receivers as arranged for a pan and furnace, with a small coke-tower to finish with.

The advantages of the system of jars are, that there is a large cooling-surface, and that the stock of acid present in them is to some extent a regulator for the variations in the supply of acid gases, which variations in most methods of decomposing salt are a very serious difficulty in the way of rational condensation; in continuous processes, like Hargreaves' direct saltcake process, or Mactear's mechanical decomposing pan, the case is different. These advantages are to some extent shared by the stone cisterns described above, but the stoneware receivers of the *bombonne* kind are superior to them in this respect, that their far more extended surface and

thinner walls secure a better cooling by air, and that they produce a more regular flow of liquid and gas in opposite directions. They are therefore better adapted than the stone tanks for producing the maximum quantity of *strong* acid, testing from 32 to 36°Tw., according to the season, and on this account are preferred by many manufacturers, while others, and nearly all the British ones, prefer the stone cisterns as being less liable to cracking, to escape from the joints, and to other troubles in keeping them in order. For that reason many English manufacturers reject even the cisterns, and confine themselves exclusively to large coke-towers, but they cannot easily bring up their acid beyond 28°Tw.

Neither stone tanks nor even a very long row of jars attain the object of *completely* condensing the HCl contained in the gases. When the percentage of HCl in the gas has become very small, the area of contact with water, as offered in that kind of apparatus, is much too restricted to be wholly efficient; the stream of gas sweeping over

the surface of the liquid yields to it but very little more of acid, and the gas leaving the row of tanks or receivers contains far more hydrogen chloride than is compatible with the requirement of preventing an undue pollution of the atmosphere. This had been recognised long before the law had interfered to establish a limit to the escape of HCl, and a solution of the difficulty had been found in the system of *coke-towers*. By these a practically complete condensation is effected, with or without the co-operation of tanks or jars; but the latter is always desirable

where acid of great and uniform strength is sought to be obtained, especially for sale. Such towers are usually known by the name of *condensers*.

Coke-towers are erections of stone, more rarely of bricks or of acid-proof stoneware, in the shape of perpendicular shafts, mostly (except with pipes) of a square (for very wide towers of an octagonal) section, and of somewhat considerable height, varying from about 40 to as much as 100 feet. The sectional area in the case of square stone or brick towers is rarely less than  $5 \times 5$  feet,

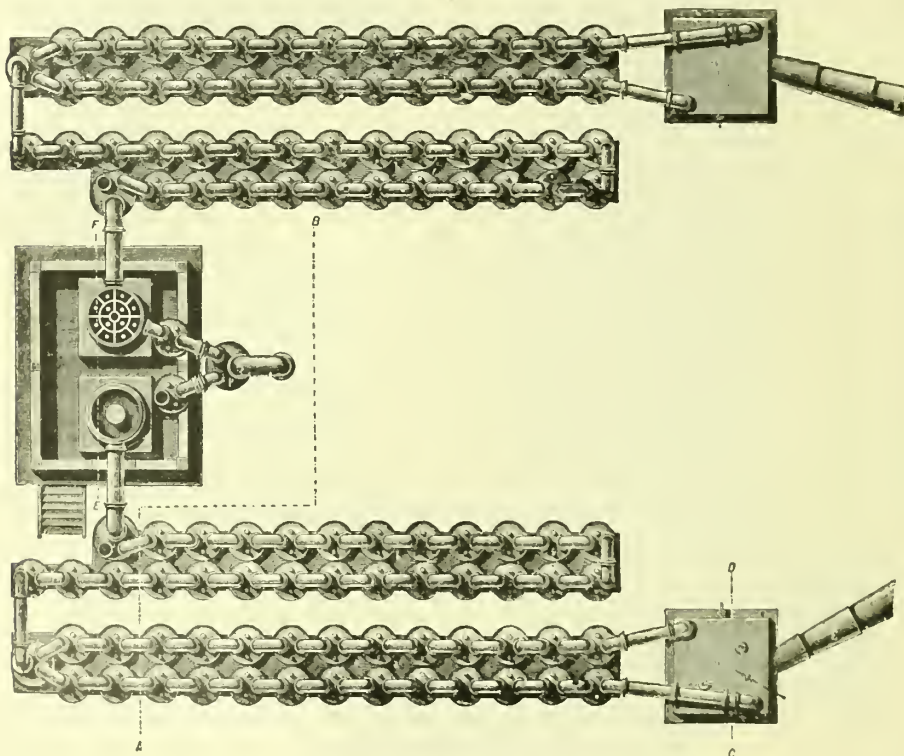


FIG. 21.

or more than  $7 \times 7$  feet; but recently they have been made up to 14 feet diameter, of octagonal shape. They are provided with a grating a few feet over the bottom, on which rests the coke which forms the 'packing' of the tower. This coke, which must be of as hard a quality as possible (only the best oven-coke is applicable for this purpose), is disposed in such a way that the gas is as much as possible divided in a large number of channels (none of them being so wide that the bulk of the gas can pass up through it), and that the current of gas is constantly deviated in this course. For this object long pieces of coke are laid parallel in a row; the next row is made to cross the lower one, and so forth. The size of the pieces is gradually diminished from bottom to top. It is also suitable to place the largest pieces outside, and smaller pieces towards the centre of the tower, where there is less friction against the sides, and the current of gas moves

more quickly. By this arrangement there is effected both a great division and constant mixture of the gases, and at the same time a suitable spreading of the feeding-water over a very large surface. The water (or sometimes weak acid) is fed in at the top by some contrivance assuring a uniform distribution over the whole area of the tower; and in dropping down it keeps the irregular surfaces of the coke moist all over, thus presenting a very large area of contact between the gases and the liquid. In consequence of the large area of the tower and the long and circuitous way the gases have to make through it, they are ultimately deprived of all their soluble parts, consisting principally of hydrochloric acid, and leave the tower in a state fit to be discharged into the atmosphere without any damage to the neighbourhood.

It is, however, necessary that a condenser should fulfil certain conditions, if it is to do its

work properly. In the first instance its size must be proportionate to the work done; if the gases pass too rapidly through it, there will not be time enough to effect a complete washing out of the acids. But it is hardly possible to lay down a strict rule as to the minimum of condensing space for a given quantity of salt decomposed. At some works a condenser  $5 \times 5 \times 59$  feet serves two pans and acts better than that of another works, where each single pan is provided with a condenser of the same size. Everything depends upon the way in which the condenser is packed, on the regularity of work in the pan and furnaces, on the proper regulation of the feed, on the draught, even upon the outward atmospheric conditions; and it is unnecessary to say that nothing like the same amount of condensing-space in the shape of coke-towers is required if the main work of condensation has been previously done by cooling-pipes or flues, cooling-towers, acid-tanks, and Woulffe's bottles.

Of recent years (*v. supra*) there has been a growing tendency in England to do away with all cooling-pipes, cisterns, wash-towers, &c., and to adopt the system of very large stone towers to do the whole work of condensation for two or even more pots and furnaces. Such towers are made hexagonal or octagonal in shape, from 10 to 14 feet diameter, and from 45 to 70 feet high, and these, with very hot gases and a single condensing shaft are found to be very efficient, condensing up to  $99\frac{1}{2}$  p.c. of the hydrochloric acid made. There is such a condenser at the Weston works, which, without cooling-pipes or other adjuncts, condenses the gases from five saltcake pots and furnaces, decomposing 300 to 320 tons per week. The escape from it is 0.10 to 0.15 grams HCl per cubic foot; the acid made by it stands  $28^{\circ}$  Tw. cold.

Of two condensing plants, one of which was provided with 320 feet length of 12-inch glass cooling-pipes, and a condensing space in the shape of a coke-tower of about 50 cubic feet per ton of salt per week, while the second plant, without any cooling-pipes, had 66 cubic feet per ton of salt per week, the second acted at least as well as the first. The last-mentioned cubic space is certainly sufficient for all purposes, for condensing the acid from both pots and roasters.

*Brick towers* are not to be recommended, as it is next to impossible to keep the numerous joints tight against acid oozing out. *Columns of stoneware pipes* cannot be made of a large area, and, therefore, are not very well adapted to large works, at least if intended for coke-towers; but they do very good service at smaller works, or as supplementary to a large condensing plant of stoneware receivers, or if provided with more efficient 'packing' than coke (*v. infra*). The material mostly employed for coke-towers is acid-proof sandstone or, in France, volvic lava, just as for acid-tanks (*cf. supra*). The system of joining the flags together is the same as shown in figs. 16 and 17 or fig. 18, but there is also another system shown in fig. 22, in which the flags are kept together by means of grooves worked in the stone, and without the aid of any ironwork, which is always a source of anxiety in acid-condensers.

The coke-towers are generally placed at a high level, and are, if necessary for this purpose,

put upon high pillars, for the purpose of running the acid from them by natural gravitation either into chlorine stills, or first, through the acid-tanks or receivers, and only then to the stills or into store cisterns for sale. They must of course have a very secure foundation, in the construction of which not merely the great weight of the tower must be considered, but also the probability that there will be now and then leakages of acid which may soften the ground and make the foundation unsafe. This can be avoided by asphaltting the ground in such a way that any

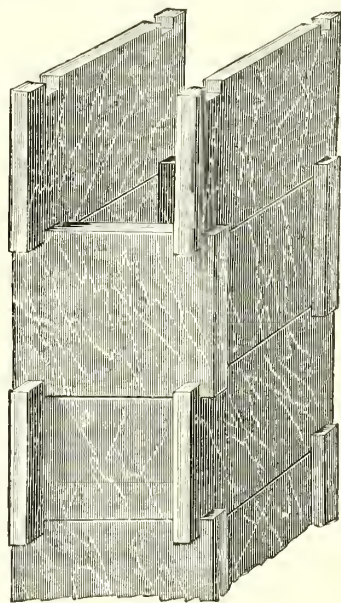


FIG. 22.

acid running down cannot penetrate into the soil, and is conveyed to a safe distance. Any damage done to the foundation, even if it amounts to much less than would cause the erection to break down altogether, is extremely injurious, because it will almost unavoidably lead to the tower getting out of level, in which case the gases will always tend to rise on the higher side, and the water will principally descend on the lower side; thus the necessary contact is not attained, and the action of the condenser is most injuriously affected.

Sometimes two condensing towers are connected; but it is not advisable to do this in such way that the gas rises in one and descends in another, for in this case the gas and the water in the second tower must travel in the same direction, which is not at all good for their intimate contact. In this case we miss the salutary action of opposite streams of gas and liquid explained above in connection with the 'bombonnes' system. The two towers should, therefore, be connected in such way that the gas, ascending the first tower, is conveyed downwards in a pipe and is made to ascend in the second tower as well.



The condensers are often left without any connection with a chimney, and then act as chimneys themselves; this is especially frequently done with pan condensers. But it is preferable to connect them with a powerful chimney, and to regulate the draught by similar means to those employed for vitriol chambers. In this case the analytical control of the escape, being effected near the ground level, is much easier to keep up to the standard of efficiency.

It has been already stated that the *feeding of the condenser with water* must take place in such manner as to supply the whole area of it with moisture. This can be done in various ways. The plan formerly considered as most efficient is that of a distributing wheel (shown in figs. 23 and 24), worked by the pressure of the feed-water itself. This causes the stream of water to reach successively every one of the holes on the top of the condenser, and thus secures a uniform action, without depending upon the top of the tower

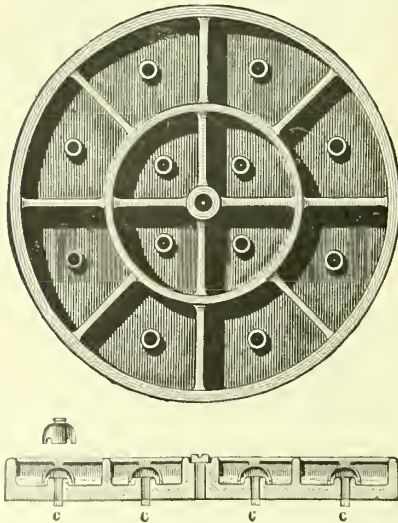


FIG. 23.

being at a mathematical level. Recently most manufacturers have done away with these acid-wheels, and have introduced troughs provided with a number of overflows all at the same level, feeding the same number of 'lutes,' c, c.

Sometimes other materials are substituted for coke as a packing of condensers. In the case of the gases of open roasters fired with coal, a coke packing would soon be stopped up with soot; in this case the condensers are loosely packed with bricks, which leave sufficient spaces between them, and which can be cleaned by flushing them out with a stream of water, but only weak acid can be obtained in this way. On the other hand, many inventors have tried to substitute for coke a packing made of earthenware, moulded in special shapes, but these attempts were usually not made in a very rational way, and were soon given up. The most recent form of apparatus intended for replacing coke-towers is the 'plate-column' of Lunge and Rohrmann, shown in fig. 25 in sections; fig. 26 shows a piece of one of the plates as seen from

above, on a larger scale; and fig. 27 the same in section.

It consists of an erection of earthenware pipes, A, B, C, filled with a series of perforated

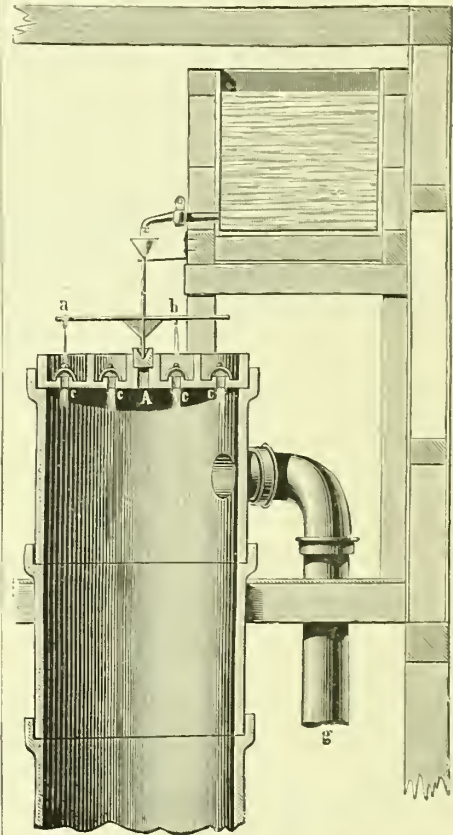


FIG. 24.

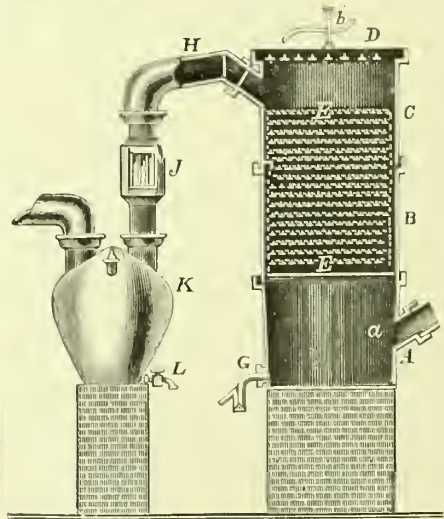


FIG. 25.

plates, *v. v.*, the perforations being made to alternate in successive plates, so that each hole corresponds to a solid place in the plates just above and below. The plates are covered with a

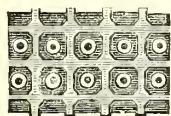


FIG. 26.



FIG. 27.

network of small ledges, so that each hole is in the centre of a minute cistern, as shown in fig. 26. The rim of the holes is somewhat raised, but not as high as the square ledges. This arrangement has the following action. The water, fed on the top by the distributing arrangement *v.*, forms a very shallow layer (about  $\frac{1}{8}$  inch deep) in every one of the tiny basins formed by the network of ledges. The water dropping down from above forces the contents of each small basin through the hole, where it forms a drop, which, on falling down, meets the point of union of four small basins, and, in splashing about, forces their contents through the four respective holes on to the plate next below, and so forth. Thus each plate is kept moistened with a continuously renewed surface of water, standing in a very shallow layer upon it, and adhering to the sides of the holes and the bottom of the plates as well. The ascending gases are divided into very many (more than 1,000) small and perfectly equal jets, which must change their direction with each successive plate, owing to the alternation of the holes. This, as well as the innumerable shocks the gases suffer in issuing from the holes of one plate against the solid plates of the next higher plate, produces an incessant intimate mixture of the gases. No false channels can exist here in which the gases and liquids can travel separately without coming into proper contact with each other, such as are never absent in coke towers. Thus the most favourable conditions are produced for a mutual action of the gaseous and liquid substances, and in consequence of this the condensation takes place in a fraction of the space required for a coke condenser. Such plate-columns are best put behind a certain number of tanks or jars, in which the gases are well cooled beforehand, and the bulk of the acid is condensed. The remainder being taken out in the plate columns, the acid condensed in these is made to flow through the tanks or jars, and is got up to strength here.

At some works, *wash towers* or 'post-condensers' are used—that is, special condensing towers, in which the gases are subjected to a final washing before issuing into the atmosphere. The acid made here is too weak for any practical use, and is mostly run away. Sometimes it is pumped up, and used for feeding the proper condensing towers, but it is always a troublesome process to pump a substance like hydrochloric acid, even in a diluted state. Under ordinary circumstances no post-condensers ought to be required at all, especially if the bulk of the acid is condensed beforehand in tanks or stoneware receivers; the work put upon the condensing towers is not too much to be fully

done in them, and the acid flowing away from them, although too weak for direct use, is brought up to full strength in the tanks or receivers, so that no weak acid whatever need be run away, as we have seen above when mentioning the recent large-sized kind of condensers.

The working of the condensing plant is far the easiest where the evolution of gas is continuous and going on at an even pace, as in the Hargreaves process or with Mactear's furnaces. In this case the feed of water need only be set once for all, and no further supervision is necessary. This regularity of work makes condensation a comparatively easy task in the above cases, although there all the HCl is greatly diluted with inert gases. It is very different with ordinary saltcake pans and furnaces, where most of the gas comes off at the first stage of the process, and the percentage of HCl in the gas presents very great variations. The feed of water must be frequently altered to suit these changes, and the case would be even worse if the somewhat large quantity of liquid contained in the condensers and tanks did not act as a regulator.

Of course a constant control must be exercised in order to satisfy the requirements of the law. The exits of the condensers, where these are not connected with a chimney, the connecting pipes with the chimney, where such exist, and ultimately the chimneys themselves, must be tested at least once a day, but preferably by a continuously acting aspirator, in order to ascertain the amount of acid escaping, distinguishing between HCl and SO<sub>2</sub>. The rules laid down by the Alkali Makers' Association for this purpose are as follows. A continuous test over 24 hours in one chimney, with intermittent daily bellows test at nine o'clock, or other specified time, to be taken and recorded. The observing apparatus to consist of three bottles or tubes, containing not less than 100 c.c. of absorbing liquid of a depth of 3 inches in each. The aperture of the inlet tube of the first bottle not to exceed  $\frac{1}{32}$  inch in diameter, of the second and third  $\frac{1}{50}$ . Absorbing liquid: water free from chlorides, speed of aspiration, as near as possible,  $\frac{1}{5}$  cubic foot per hour. Mode of testing: decinormal silver nitrate (10.8 gram Ag per litre), with chromate indicator. The variations of temperature and barometric pressure to be noted, and corrections made to 60°F. and 30 inches Bar. The results to be stated in grains per cubic foot.<sup>1</sup> To this the remark must be made that the chromate indicator does not act when SO<sub>2</sub> occurs in the gas, as is frequently the case; this can be remedied by oxidising the SO<sub>2</sub> by means of potassium permanganate.

The yield of hydrochloric acid, at the very best conducted works, is 148 parts of acid, standing at 34 to 36°Tw. (1.70 to 1.80 sp.gr.) for 100 parts of saltcake. This is very nearly the theoretical yield, and at most works a smaller quantity—say, 140 or 130 parts—of strong acid is made.

The concentration of the acid varies both with the construction of the apparatus and with the season. With coke condensers alone it is difficult to make acid above 28°, or at most 0°Tw., even from pan-gas, and in winter;

<sup>1</sup> For more exact prescriptions see Lunge and Hurter's Alkali Makers' Pocket Book, 191 and 195.



but where tanks or jars are provided, not merely the pan-gas, but even the gas from close roasters, is made to yield acid of  $36^{\circ}\text{Tw.}$  in the cold season, and some get up to  $38^{\circ}\text{Tw.}$  In summer it is difficult to exceed  $34^{\circ}$ , but the strength ought not to fall below  $32^{\circ}\text{Tw.}$  (measured at  $15^{\circ}\text{C.}$ ). The gas from open roasters is rarely made above  $24^{\circ}$  or  $26^{\circ}\text{Tw.}$ , even where they are fired with coke; and when firing them with coals the acid obtained is only  $2^{\circ}$  or  $3^{\circ}$  strong.

The impurities found in commercial hydrochloric acid are, chiefly, sulphuric acid, ferric chloride, arsenic, and either free chlorine or sulphurous acid. The acid condensed from the pan gas is always much purer than that from the roaster gas. The quantity of sulphuric acid sometimes amounts to 2 p.c. and upwards; it is very troublesome in the Weldon, and even more in the Deacon, chlorine process and in some other applications of hydrochloric acid. Most of it can be kept out by employing a small 'cooling tower,' as described above; and its complete removal is easily effected by a cautious addition of barium chloride, in which case the precipitated barium sulphate, if collected in a clean state, forms a saleable by-product as a white paint for staining wall-papers, &c. Even calcium chloride removes much of the sulphuric acid—sufficiently so for the Weldon process (Strype's Patent, 1882).

The following proposals have been made for removing the sulphuric acid from the hydrochloric acid during the condensation itself, or immediately after, in order to utilise the roaster acid—otherwise not suitable for the Deacon process—for this cheap mode of obtaining chlorine.

Solvay passes the impure gases into a concentrated solution of calcium chloride, which retains the hydrochloric acid as well as the sulphuric acid, and allows the inert gases to pass away. On heating the solution, pure HCl is given off, and can be used as such. This is greatly promoted by passing a stream of air through the hot solution, the mixture of air and HCl being very suitable for the Deacon process.

Hasenclever (E. P. 3,393 of 1883) mixes the impure acid, previously condensed, with hot sulphuric acid, and accelerates the liberation of HCl by blowing in air or stirring. The diluted sulphuric acid is used over again after being concentrated by evaporation. This process is also especially adapted to the Deacon process, and seems to be very successful; but it involves the concentration of a very large amount of sulphuric acid.

Lunge and Naef (1887) attain the same end by blowing hot air or roaster gas through the previously heated impure acid, thus volatilising pure HCl along with the air required to convert it into chlorine by Deacon's process.

Deacon and Hurter (1889) pass the impure gases through rock salt, which causes the sulphuric acid to be retained in the shape of sulphate of soda, HCl being given off.

Arsenic gets into the hydrochloric acid through the sulphuric acid employed in its manufacture; the arsenic is thereby converted into  $\text{AsCl}_3$ , and passes as such into the condensing apparatus. Many plans have been proposed for its removal—most frequently a treatment with sulphuretted hydrogen or with sulphides.

Bettendorf (D. P. J. 194, 253) precipitates the arsenic from concentrated hydrochloric acid by stannous chloride, distilling it afterwards. Dulos dilutes the acid to sp.gr. 1.13, and digests it with strips of sheet copper at  $30^{\circ}\text{C.}$  for twenty-four hours, and repeats this treatment with freshly scoured copper. This removes all the arsenic and the free chlorine, and reduces the ferric chloride to ferrous chloride, which remains behind on distillation. Beckurts (Fischer's Jahresb. 1884, 348) distils hydrochloric acid with ferrous chloride and removes the first 30 p.c. containing all the arsenic.

Even selenium is sometimes found in such quantities in hydrochloric acid as to be troublesome in its application (Davis, S. C. I. 1883, 157).

#### HYDROCHLORIC ACID FROM OTHER SOURCES THAN THE LEBLANC PROCESS.

*Hydrochloric acid from calcium chloride.*  
In connection with the ammonia-soda process, in which the chlorine of the salt passes into the state of calcium chloride, very many proposals have been made for treating the latter substance so as to obtain HCl therefrom. Most of these have at the same time for their object the direct production of free chlorine, and the hydrochloric acid is in this case merely an accidental, but unavoidable, by-product. (These processes are described earlier in this article.) In this place we mention only some of the proposals for obtaining HCl from  $\text{CaCl}_2$ , none of which has had any practical success.

Solvay treats calcium chloride, mixed with silica or aluminium silicates, in a current of superheated steam (Patents of 1877 and following years).

*Hydrochloric acid from magnesium chloride.*  
This salt, which occurs in enormous quantities as a waste product of the Stassfurt potassium industry (200,000 tons in 1887), and which is sometimes obtained as a by-product in other technical operations, yields very much hydrogen chloride when its solution is concentrated beyond the point where the compound  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  would be formed. Both the production of hydrochloric acid and the direct production of chlorine from magnesium chloride have been the object of innumerable attempts, a synopsis of which is given by Eschellmann in *Chemische Industrie*, 1889, 2, *et seq.* He also describes there an extended series of laboratory experiments by which he studied the decomposition of  $\text{MgCl}_2 + \text{H}_2\text{O}$  into  $\text{MgO} + 2\text{HCl}$ . It is well known that the reaction is not as simple as is represented by that equation, a large quantity of magnesium oxychloride being formed. On heating the liquor up to  $250^{\circ}\text{C.}$  just one-third of the HCl is set free, and up to  $350^{\circ}\text{C.}$  the action proceeds no further. Above that temperature the decomposition sets in again, and at about  $550^{\circ}$  half of the HCl has been removed, leaving a residuum of the composition  $\text{MgO} \cdot \text{MgCl}_2$ . A complete decomposition can be produced only by supplying more steam, since all the water is driven out long before driving out the HCl. This can be produced in one of the following ways:—

1. Heating the  $\text{MgCl}_2$  gas from without, and introducing superheated steam into the heated salt. This was patented in various ways—by Clemm in 1864, Weldon in 1871, Heinzerling and Schmid in 1887. This admits of easy con-



densation of the HCl, but heating from without is hardly practicable, and the contact between the steam and the salt is never intimate enough.

2. Mixing the  $\text{MgCl}_2 \cdot 6\text{aq}$  with such salts as lose their water only at a high temperature, heating that mixture, and ultimately recovering the salts employed.

This was attempted by Eschellmann (1881) with the aid of Kieserite or Epsom salts; by Konther (1887) with calcium chloride. The expense is, however, too great.

3. Heating the  $\text{MgCl}_2 \cdot 6\text{aq}$  by a direct flame, employing either coal containing much water or directly mixing steam with the products of the combustion of fuel.

To this class belong the patents of Solvay (1877-1888), Randohr (1879), Weldon (1881), Randohr and Blumenthal (1881), Vogt (1885), Salzbergwerk Neustassfurt (1885 and 1888). The advantage in this case is the economical use of the heat by the direct contact of the fuel gases with the magnesium chloride; but there is the great drawback that the HCl is mixed with a large amount of impurities and inert gases, and its condensation to pure strong acid is very difficult of attainment. Most of these patents refer at the same time to a direct production of chlorine, by means of an oxidising flame, and some of them to the production of magnesia as a technical product. As a means of manufacturing hydrochloric acid by itself, none of these processes can compete with the ordinary Leblanc process. The most promising of all new processes, that of Weldon and Péchiney, is not intended for hydrochloric acid, but for chlorine, where description of it will be found.

Other Stassfurt products, the minerals *canallite* and *kainite*, are the subject of a patent of Solvay's (1888), who recovers from them both HCl and Cl by the same means as he employs for calcium chloride (*cf. supra*).

*Hydrochloric acid from the ammonium chloride of the ammoniac-soda process* (*cf. this for many details*). Mond (1883) heats the ammonium chloride with so much sulphuric acid that the acid sulphate is formed and all HCl is expelled. The acid sulphate is converted by means of ammoniacal vapours into the neutral salt of commerce. O. N. Witt (1886) expels the HCl from  $\text{NH}_4\text{Cl}$  by means of syrupy phosphoric acid, which forms ammonium phosphate. On heating this at a higher temperature, the ammonia is driven out as well, and the phosphoric acid is regenerated. Jurisch (D. P. J. 267, 431) has shown that this process is not practicable, because there is no material known which resists the fusing phosphoric acid, and only 63 to 86 p.c. of the  $\text{NH}_3$  is recovered.

Mond passes the vapour of ammonium chloride over nickel oxide, heated to at least  $350^\circ\text{C}$ ., which absorbs the HCl and allows the  $\text{NH}_3$  to pass on. After a certain time the process is changed by raising the temperature to  $500^\circ$  or  $600^\circ\text{C}$ . and decomposing the nickel chloride by steam, when HCl is driven off and NiO regenerated. (Several patents taken out in 1886.)

The conveyance of hydrochloric acid mostly takes place in glass carboys with basket or wire hampers, sometimes in earthenware carboys of the same size (about 10 or 12 gallons). Gutta pereha vessels, which were formerly in use at

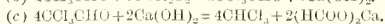
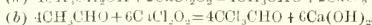
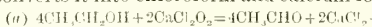
some places, have been discontinued on account of their great expense. At some manufactories in Germany the acid makers employ for railway transit very large earthenware jars, holding about a ton each, supported by somewhat elastic woodwork, in order to resist the unavoidable shocks in shunting &c. Ebonite tanks have also been used occasionally. At a large French works they use iron cylinders, lined with ebonite, holding eight tons each, with great success.

The applications of hydrochloric acid are very numerous, but most of it serves for producing chlorine. The acid is, moreover, used for preparing the chlorides of various metals, for extracting the phosphates from bones &c., for purifying bone-char (it must be quite free from sulphuric acid for this purpose), in dyeing and tissue-printing, for preparing carbonic acid, for neutralising the alkaline "melts" in the manufacture of alizarin, resorcin, &c., in manufacturing many other coal-tar colours, for recovering sulphur from alkali waste by Mond's and Schaffner's process (now obsolete), and for innumerable other purposes. G. L.

#### CHLOROFORM *Trichloromethane* $\text{CHCl}_3$ .

Chloroform was discovered by Liebig in 1831 (P. 23, 442), and independently, about the same time, by Soubeiran (A. Ch. [2], 48, 131). Besides its well-known use as an anæsthetic, for which purpose it was introduced by Simpson in 1848 (Edin. Monthly J. Med. Sc. 8, 415), it is largely employed as a solvent in chemical manufactures. It is also a valuable antiseptic, and in medicine its applications are numerous, especially in the case of spasmodic diseases.

*Formation*.—1. By the action of alkalis on chloral  $\text{CCl}_3\text{CHO} + \text{NaHO} = \text{CHCl}_3 + \text{HCOONa}$  (Liebig, P. 23, 442; A. 1, 199; 162, 161).—2. By acting on alcohol with bleaching powder. The hypochlorite of the bleaching powder probably, in the first instance, converts the alcohol into aldehyde, then into chloral, liberating calcium hydroxide, which latter, reacting on the chloral, converts it into chloroform and calcium formate:

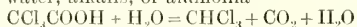


(Liebig; Soubeiran, A. Ch. [2] 48, 131; Soubeiran a. Mialhé, A. 71, 225). A very similar reaction takes place when a mixture of alcohol and an alkaline chloride is submitted to electrolysis, whereby chloroform is also produced (Patent, S. C. I. 1885, 243). Methylic cannot be substituted for ethylic alcohol in these processes, for it yields no chloroform when treated with bleaching powder (Belohoubek, A. 165, 349).—3. Chloroform is produced by the action of chlorine or bleaching powder on acetone or acetic acid (Liebig) or acetophenone (Orndorff, A. Jessel, Am. 10, 363).

With acetone the reaction is

$$2\text{CO}(\text{CH}_3)_2 + 6\text{CaOCl}_2 = 2\text{CHCl}_3 + 2\text{Ca}(\text{OH})_2 + 3\text{CaCl}_2 + (\text{CH}_3\text{COO})_2\text{Ca}$$

(O. a. J.).—4. By heating trichloroacetic acid with water, alkalis, or ammonia



(Dumas, A. Ch. [2] 56, 115; A. 32, 101; Beckurts a. Otto, B. 14, 589).—5. Chloroform is also produced by reacting upon turpentine and the terpenes with bleaching powder (Chautard, J. 1851, 501).—6. By the action of nascent hydrogen on carbon tetrachloride (Geuther, A. 107, 212).—

7. Together with methylene chloride by treatment of methyl chloride with chlorine in sunlight (Regnault, A. 33, 328).—8. From iodoform by the action of phosphorus pentachloride (Gautier, Bl. [2] 13, 127).

*Manufacture.*—Chloroform is chiefly prepared by distilling a mixture of bleaching powder, water, and alcohol, with or without the addition of slaked lime. The diluted alcohol is warmed in a still to which a condenser is attached, and then the bleaching powder and lime is added, and the temperature raised till chloroform begins to come over, after which the heat evolved by the reaction itself suffices to complete the distillation. Sometimes an evolution of oxygen has been noticed during the progress of the reaction. This arises from decomposition of part of the hypochlorite by heat (Bechamp, A. Ch. [5] 22, 347). Operators differ as to the best proportions of alcohol and bleaching powder to be employed (*cf.* Kessler, J. Ph. [3] 13, 162; Simmerling, Ar. Ph. [2] 53, 23; Belohoubek, *l.c.*; Brit. Pharm. 1885, 108). For small quantities the directions of the Pharmacopœia may be followed. The apparatus used for manufacturing on a larger scale usually consists of a generator with an attached condenser and receiver, a washing apparatus and tanks, all made of iron, and a copper still for the final rectification (*cf.* Chem. Z. 10, 338). The generator is cylindrical, 1.4 m. high, and 2 m. in diameter, and is constructed of boiler plate 13–14 mm. in thickness. It is fitted with an agitator, a man-hole through which the charge is introduced, a tube 75 cm. in diameter connecting with the condenser, and two other tubes, the one for the introduction of water and the other for steam. A tube passes through the plate at one place closed at the lower end and filled with oil to hold a thermometer. There is also arranged, outside the generator, a leaden tube connected with the water supply, by which a small current of water can be spread over the generator when, as sometimes occurs, the temperature of the reaction rises too high. The tube leading to the condenser should be short, and should have as great a dip as possible. Between the condenser and the receiver is inserted a piece of glass tubing, by means of which the evolution of chloroform may be observed. The receiver is a cylindrical tank made of boiler-plate about 15 mm. in thickness and is about 75 cm. high and 40 cm. in diameter. The washing apparatus consists of a narrow high cylinder with a rounded bottom in which is fitted an agitator in the shape of a ship's screw. This, when working, keeps up a movement of the liquid from below upwards. Taps are placed in the sides to draw off the alcoholic washings. The final rectification is conducted in a copper still, the arm of which leading to the condenser is made as short as possible.

Three parts of 85 p.c. alcohol diluted with 60 parts of water are added to the generator, and then, while the agitator is in motion, 12 parts of bleaching powder, which should contain not less than 35 p.c. of available chlorine. Steam is applied till a temperature of 40° is obtained, when it is shut off. The temperature still rising, the agitator is stopped when about 45° are indicated, after which the heat of the reaction causes a further increase in temperature which

generally does not exceed 60°. If it should rise higher than 60° the cooling apparatus must be made use of. The beginning of the reaction is marked by a fine rain of chloroform, alcohol and water being driven rapidly through the condenser tube, and the air contained in the apparatus being energetically expelled. The chloroform soon follows, the agitator being set in motion to assist towards the close of the distillation. When the product on being examined ceases to separate in layers, when, in fact, it consists of a solution of chloroform in alcohol, it should be collected separately. This is continued until, on the addition of water to the distillate, no further separation of chloroform takes place. After the chloroform has all come over a quantity of weak spirit is recovered. The crude chloroform is then thoroughly washed in the washing apparatus, and finally rectified from the copper still. The washings, together with the various spirituous distillates, are utilised in subsequent operations (*cf.* Ch. Z. 10, 338).

In England chloroform is prepared not only from 'rectified spirit,' but also from the duty-free 'methylated spirit,' a mixture of rectified spirit with 10 p.c. of wood naphtha. The latter product can be sold at a much lower price than the former. It has been doubted whether it is applicable to purposes of inhalation, but the weight of evidence is in favour of the view that 'methylated' chloroform when properly purified may be employed as an anæsthetic with precisely the same degree of safety as chloroform prepared from rectified spirit. Indeed, it seems impossible, either chemically or physiologically, to distinguish the one from the other.

Other reactions employed for the manufacture of chloroform are: the action of bleaching powder on acetone, of which method particulars are given with drawings of apparatus by Sadler (Ph. [3] 20, 84); the electrolysis of solutions of chlorides of the metals of the alkalis or alkaline earths in alcohol or acetone, the whole being kept heated during the operation (Patent, S. C. I. 1885, 243); and the destructive distillation of acetates, and subsequent treatment of the distillate with hypochlorite (Patent, S. C. I. 1885, 611).

The chloroform prepared by any of the above-mentioned processes is not of so high a degree of purity as that produced by the action of alkalis on previously purified chloral, and requires purification before it is adapted for purposes of inhalation. The first step is usually to wash it with water, which removes traces of ethylic alcohol. Then it is left for a short time in contact with sulphuric acid (Gregory, Pr. E. 1850, 391) which must be free from nitrous compounds (*cf.* Christison, Ph. 10, 253; Redwood, Y. B. Ph. 1870, 119). This acid has no action on chloroform itself unless the operation be unduly prolonged, but it chars most of the impurities which are commonly present. In the next place the product is allowed to stand in contact with recently ignited carbonate of sodium (*cf.* Thorpe, C. J. 37, 196) or with oxide of manganese, or it is washed with lime water and afterwards dried over chloride of calcium. In any case it is finally distilled at a temperature not above 64° (*cf.* Werner, Ar. Ph. [3] 12, 450; Thorpe, *l.c.*; Remys, Ar. Ph. [3] 5, 31; Michaelis a. Mayer, D. P. J. 261, 496). Chloro-

form is liable to decomposition in presence of air and sunlight. Among the products formed are hydrochloric acid and chlorine (Marson, Ph. 8, 69; Abraham, Ph. 10, 24), and sometimes carboxyl chloride (Regnault, J. Ph. [5] 5, 504). Such decomposed chloroform may be purified by washing with hyposulphite of sodium and subsequent distillation (Shuttleworth, Ph. [3] 3, 1016; *cf.* Remy's, Ar. Ph. [3] 5, 31). The addition of 1 p.c. of ethylic alcohol is largely practised to prevent the decomposition of chloroform (*cf.* Brit. Ph. 1885, 109; Jolles, Ch. Z. 11, 786).

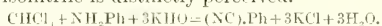
*Properties.*—Chloroform is a liquid having a sweet taste and an agreeable ethereal odour. When inhaled it produces anaesthesia. As an antiseptic it prevents the growth of micro-organisms; but does not affect the action of soluble ferments (*cf.* Patent, S. C. I. 1886, 331). For antiseptic applications *v.* Robin (C. R. 30, 52), Augendre (C. R. 31, 679), Barnes (Ph. [3] 5, 441), Salkowski (Ch. Rep. 1888, 166), also Ph. [3] 18, 315, 356 a. 855. Chloroform is very sparingly soluble in water, 1 vol. dissolves in 200 (*cf.* Chancel a. Parmentier, C. R. 100, 773). It mixes in all proportions with alcohol or ether. It may be made into an emulsion with water by means of saponin (Patent, S. C. I. 1887, 382). Sulphuric acid does not dissolve it. Chloroform is an important solvent; dissolving fats, resins, india-rubber, sulphur, phosphorus, iodine, alkaloids, many alkaloidal salts, as well as numerous other organic compounds (*cf.* Pettenkofer, J. 1858, 363; Schlimper, 1859, 405; Nowak, Ar. Ph. [3] 3, 281; Hesse, Ph. [3] 4, 649).

M.p.  $-70^{\circ}$  (Berthelot, Bl. 29, 3). B.p.  $61.2^{\circ}$  (*cor.*) (Thorpe, C. J. 37, 196; *cf.* Regnault, J. 1863, 70; Pierre, A. Ch. [3] 33, 199; Schiff, A. 220, 95). Sp.gr.  $1.52637 \frac{2}{3}$  (Thorpe, *cf.* Pierre; Schiff). V.D. 4.199 (Dumas), 4.230 (Regnault). Coefficient of expansion .0012302 (Thorpe). Chloroform is not inflammable even with a wick at ordinary temperatures. It may, however, be made to burn, with a green smoky flame, when boiling, or by means of a wick when diluted with alcohol. Heated to redness its vapour is decomposed, yielding chlorine and various chlorides (Radsky, J. pr. 46, 170; Ramsay a. Young, S. C. I. 1886, 232). By treatment with zinc and sulphuric acid, methylene chloride  $\text{CH}_2\text{Cl}_2$  is formed; with alcohol or ammonia and zinc-dust, methane (*cf.* Perkin, C. N. 18, 106); with alcoholic potash, formate and chloride (Regnault) together with carbonic oxide (Geuther, A. 123, 121), or in closed tubes, ethylene (Berthelot, A. Ch. [3] 54, 87); with alcoholic potash in presence of monamines, isonitriles (Hofmann, B. 3, 769); with sodium alcoholate, methenyltriethyl ether,  $\text{CH}(\text{OEt})_3$  (Williamson a. Kay, C. S. Mem. 7, 224); with concentrated hydriodic acid when heated, methylene iodide  $\text{CH}_2\text{I}_2$  (Lieben, Z. [2] 4, 713); with red-hot copper (Berthelot, C. R. I. 805) or potassium amalgam (Kletzinsky, Z. [2] 2, 127), acetylene  $\text{C}_2\text{H}_2$ .

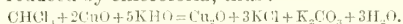
Chromic acid converts chloroform into phosphene,  $\text{COCl}_2$ . Repeatedly distilled in a current of chlorine, hydrochloric acid and carbon tetrachloride are formed (Regnault). Ordinary nitric acid has little or no action (Soubeiran), but

fuming acid in closed tubes at  $100^{\circ}$  slowly converts it into chloropicrin,  $\text{C}(\text{NO}_2)\text{Cl}_3$  (*cf.* Mills, C. J. [2] 9, 641). Bromine and iodine derivatives *v.* Paterno (G. I. 593), Friedel a. Silva (Bl. [2] 17, 537), Bolas a. Groves (C. J. 9, 779). Sodium reacts on chloroform in contact with atmospheric air, forming formate and chloride together with free carbon and other products (Kern, C. N. 31, 121). Potassium decomposes chloroform vapour with liberation of carbon and formation of chloride (Liebig; *cf.* Heintz, P. 98, 263). Caustic potash solution has no action on chloroform even when boiled with it; but heated in closed tubes formate and chloride are formed (Dumas). Similar products together with carbonic oxide are obtained by treatment of chloroform in closed tubes at  $180^{\circ}$  with ammonia and water (André, C. R. 102, 553). At a red heat ammonia reacts on chloroform, forming hydrocyanic and hydrochloric acids (*cf.* Heintz). Chloroform combines with sulphuretted hydrogen and with water at  $0^{\circ}$ , forming the crystalline compounds  $\text{CHCl}_3(\text{H}_2\text{S})_2(\text{H}_2\text{O})_{23}$  (Loir, J. 1852, 560; Forcrand, A. Ch. [5] 28, 12); and  $\text{CHCl}_3(\text{H}_2\text{O})_{18}$  (Chancel a. Parmentier, C. R. 100, 27).

The following reactions have been made use of in the detection or estimation of chloroform:—1. The reaction between chloroform and monamines in presence of alcoholic potash. A small portion of the liquid to be tested is added to a mixture of a monamine, anilin for instance, together with some alcoholic potash, and heat applied, when it traces even of chloroform are present, the characteristic disagreeable odour of an isonitrile is distinctly perceived.



This test, which serves to distinguish one part of chloroform in 5,000–6,000 of alcohol, further distinguishes between chloroform and its allied derivatives such as ethylidene chloride  $\text{CH}_2\text{CHCl}_2$  (Hofmann, B. 3, 769).—2. A delicate colour reaction takes place between potassium phenate and chloroform. An alcoholic solution of phenol is mixed with caustic potash and evaporated to dryness. If chloroform be now added a splendid red-purple colour is developed (Guareschi, G. 1873, 401; Raupenstrauch, Ph. [3] 19, 668).—3. If chloroform be added to a solution of caustic soda with an excess of resorcinol and heat be applied to boiling, a yellow-red colour is developed which when largely diluted shows a yellowish-green fluorescence (Schwarz, Fr. 27, 668; Raupenstrauch).—4.  $\alpha$ - or  $\beta$ -naphthol dissolved in concentrated caustic potash solution, and warmed with a little chloroform gives a rich blue liquid which changes in the air to green and brown (Lustgarten, M. 3, 715).—5. Fehling's solution is reduced by chloroform, thus:



This reaction furnishes a means of indirectly estimating chloroform (Baudrimont, J. Ph. [4] 9, 410).—6. For the estimation of chloroform in alcoholic solution *v.* Thresh (Ph. [3] 11, 319).—7. Chloroform is detected in blood by distillation from a water bath, and its decomposition into chlorine and other products when the gases evolved are led through a tube heated to redness. The liberation of chlorine is observed by its action on starch and iodide of potassium paper. (Ragsky, *L.c.*; Duroy, J. Ph. [3] 20, 401; Ludeking, C. N. 55, 149).—8. To detect it in



cases of fatal poisoning Vitali distils the intestines and passes hydrogen through the distillate. The hydrogen, carrying with it portions of any chloroform which may be present, is burned at a jet and in the flame is fixed a copper wire. Very minute quantities of chloroform generate hydrochloric in the flame sufficient to act on the copper and impart a bright green colour (*Giorn. Farm. Ch.* 30, 529).—9. For applications of the naphthol colour test to forensic analysis *v. Lustgarten (l.c.)*.

**Detection of impurities.**—Chloroform for inhalation should leave no residue or unpleasant odour on evaporation, should be neutral to test-paper, and give no indication of hydrochloric acid when tested with nitrate of silver. A much more delicate method of detecting free acid is to add to 5 c.c. of chloroform 1 drop of a solution of phenolphthalein and 1 drop of a centinormal solution of caustic potash with 1 c.c. of water. The mixture is shaken and set aside. If free from acid the red colour should not disappear in twenty-four hours (*Valpius, Ar. Ph.* [3] 25, 998). The presence of alcohol in chloroform may be detected by the darkening in colour of sulphuric acid shaken with it (*Gregory, Pr. E.* 1850, 391); by the formation of iodoform (*Hager, Ph.* [3] 1, 683); by the tint of the solution which it gives with iodine (*Siebold, Ph.* [3] 10, 213); by the addition of Hofmann's violet which is quite insoluble in pure chloroform (*Regnaud, J. Ph.* [4] 29, 402); by its reducing action on an alkaline solution of potassium permanganate (*Xvon, J. Ph.* [5] 5, 225) or manganate (*Jolles, Ch. Z.* 11, 786 a. 1391), or on chromic acid (*Cottell, J. Ph.* [3] 13, 359). The fact that chloroform for inhalation purposes usually contains alcohol, purposely added to increase its stability, materially lessens the value of these tests in practice (*cf. Dott, Ph.* [3] 12, 769). Aldehyde may be detected by many of the tests for ethylic alcohol, and also by warming with potash, when its presence is indicated by a darkening in colour (*cf. Regnaud, l.c.; Scholvién, Ph. Z.* 32, 686). A. S.

**CHOLESTERIN**  $C_{26}H_{44}O$ . Discovered by Conradi in 1775 in gall-stones. Found in human bile, in blood, and in the brain; in epidermis and in hair; also present in various morbid products of the animal body, *e.g.* cerebral concretions, scirrhus matter of the mesocolon, hydropic liquid of the stomach, testicles, &c. Also found in horn and hoofs; in whalebone, tortoise-shell, feathers and bristles, &c. Its most abundant source is, however, the fat of greasy wool (wool grease), in which it was first detected by Hartmann and Schulze.

Cholesterin may be detected in fats &c. by dissolving the substance in acetic anhydride and adding concentrated sulphuric acid, when the solution becomes first pink and eventually blue.

Cholesterin crystallises in thin white nacreous monoclinic lamina: m.p.  $115^{\circ}$  and of sp.gr. 1.067. Has a neutral reaction, and is without taste or smell; insoluble in water; sparingly soluble in cold but readily dissolved by boiling alcohol. Also soluble in ether, chloroform, acetone, wood spirit, benzene, oil of turpentine, and in the neutral fats and fatty acids. Sublimes unchanged at  $200^{\circ}$ , but is decomposed at a higher temperature. Cholesterin appears to be an alcohol homologous with cinnamic alcohol, and com-

bines with the fatty acids, forming esters or compound ethers similar to the glycerides.

This substance is found in commerce under the name of lanolin, and is used mainly for medicinal purposes, and, owing to the ease with which it is absorbed by the skin, as a substitute for vaseline, lard, or in the composition of plasters, ointments, and salves. Has also been employed in the manufacture of cosmetics and pomades, and for softening leather. Lanolin is obtained from wool-oil, which contains about 70 p.c. of cholesterin and 30 p.c. fatty acids, by saponification by means of caustic soda, whereby an emulsion is obtained which on dilution with water gives so-called 'wool-milk.' On treatment in a centrifugal machine impure lanolin separates out as a cream, and may be precipitated by lime. The purified product is afterwards kneaded with about 30 p.c. of water, in which state it is found in commerce.

Anhydrous lanolin absorbs about 100 p.c. of water; does not become rancid, and is antiseptic.

**CHOLINE** *v. VEGETO-ALKALOIDS*.

**CHONDRIIN**. A substance allied to and much resembling gelatin. Obtained by boiling cartilage with water. When dried it is a hard, horny substance, which softens to a jelly in cold water, and is entirely dissolved by boiling water. It is precipitated from its aqueous solution by nearly all acids, in excess of certain of which it redissolves, and by alum, lead acetate, copper and iron sulphate, and mercuric and mercurous nitrates. These reactions are said to distinguish it from gelatin.

By Morochowitz chondrin is regarded as a mixture of gelatin, mucin, and salts (*v. GLUE*).

**CHRISTOPHITE**. A mineral from St. Agnes, Cornwall, containing 37.6 Zn, 26.2 Fe, 1.4 Sn, 34.7 S (*Collins, Min. Mag.* 1879, 91).

**CHROMATE OF LEAD** *v. LEAD*.

**CHROMATOMETERS** *v. COLORIMETERS*.

**CHROME, VIOLET**. Syn. *Mauveine*, *Perkin's violet*; *v. AZINES AND COLORING MATTERS DERIVED FROM THEM*.

**CHROMIUM**. (*Fr. Chrome*; *Ger. Chrom*.) Symbol Cr. At. w. 52.45 (Péligot, Berlin). Chromium occurs principally as chrome iron ore or *chromite*. As sesquioxide  $Cr_2O_3$  it is found in small quantities in *chrom-crore*, generally mixed with clay and associated with chromite, in France and Siberia. As chromate of lead it occurs in *crocoisite* and *malanchroite*  $PbCrO_4$ , and as a basic chromate of lead in the rare mineral *phamite*  $3PbO \cdot 2CrO_3$ . The greenish colour of the emerald, verd-antique marble, serpentine, and many other minerals, is due to the presence of chromium sesquioxide.

**Preparation.**—Metallic chromium may be prepared by several methods. Deville produced it in combination with a small quantity of carbon, in ingots weighing as much as 100 grams, by the ignition of a mixture of chromium sesquioxide and sugar in a lime crucible, at the highest temperature of a blast furnace. Thus formed it is a shining, steel-grey metal, capable of taking a good polish, sp.gr. about 5.9, as hard as corundum and less fusible than platinum (Deville). It may be heated to redness in air without change, but when heated with nitric or potassium chlorate it becomes converted into potassium chromate, in the latter

case with incandescence. It is insoluble in nitric acid or cold dilute sulphuric acid, but rapidly dissolves in the latter when heated; soluble in hydrochloric acid. When heated it combines with chlorine with incandescence.

Chromium combines with most non-metals. It decomposes steam at a red heat.

Wöhler (A. 111, 230) prepared chromium by fusing a mixture of the violet chromium sesquichloride with twice its weight of zinc under a layer of equal parts of potassium and sodium chlorides. The mixture of zinc and chromium so produced was treated with dilute nitric acid to remove the zinc, and the chromium remained as a light greenish powder consisting of minute octahedra belonging to the quadrate system (Bolley), of sp.gr. 6.81 according to Wöhler, 7.3 according to Bunsen.

When sodium amalgam is shaken up with a solution of chromous or chromic chloride or iodide, a liquid amalgam of chromium and mercury is produced. This is heated in a current of hydrogen to evaporate the mercury, and the chromium obtained as a spongy powder. Readily soluble in dilute nitric or sulphuric acids, sparingly so in hydrochloric acid. When heated on platinum foil it suddenly becomes incandescent, with the production of chromium sesquioxide (Moissan).

**Alloys.** With *aluminium* a white crystalline alloy resembling tin may be produced, by fusing in a crucible a mixture of 1 part of potassium chloride, 2 parts chromic chloride, and 1 part aluminium. The alloy produced contains about 63 p.c. of chromium and 29 p.c. of aluminium, with silicon and iron if present in the aluminium. When heated in air the alloy changes colour like steel. It is less fusible than nickel. Nitric acid or caustic alkali solution is without action upon it, but it dissolves in hydrochloric acid with evolution of hydrogen. When heated with concentrated sulphuric acid a green mass is produced, with formation of hydrogen and precipitation of sulphur, but no evolution of sulphurous oxide.

With *iron* the alloys of chromium are of great interest. The presence of chromium in iron or steel produces a much finer texture, greater hardness, tenacity, and elasticity, and greater smoothness of fracture. Chromium cannot be used to replace carbon in steel, as has been asserted (Boussingault).

When crystalline, the tendency of these alloys is to produce needles instead of plates, as in the case of manganese.

Chromium steel is usually prepared by the addition of a definite quantity of an alloy of chromium and iron of known composition. This alloy is produced by fusion in a plumbago crucible of a mixture of chrome iron ore with 6 or 8 p.c. of charcoal or anthracite under a flux of calcium or sodium fluoride and lime, or of chalk and borax, according to the amount of earthy matter present in the ore. An alloy of iron containing carbon and 15 p.c. of chromium is hard and tough, of slightly lamellar, white, silky fracture; with 25 to 30 p.c. of chromium the alloy is white and brilliant, with fine needles disseminated through the mass. When this proportion is exceeded the needles become smaller, and the metal is more brittle and less fusible,

until, with 68 p.c. of chromium, the alloy is hardly fusible at the highest temperature of a wind furnace.

The presence in steel of 2 to 4 p.c. of chromium and 1.2 to 1.4 p.c. of carbon renders it so hard, that it is bored with difficulty by good steel drills. This alloy, when tempered above redness, has a fracture resembling porcelain.

It is stated that the presence of 65 p.c. of chromium destroys the magnetic properties of iron. By fusing a mixture of 315 parts of chrome iron ore, 200 of powdered charcoal, and 70 of lime in a plumbago crucible, Sergius Kern obtained an alloy containing 74 p.c. of chromium and 25 p.c. of iron, hard enough to cut glass, and of silver-white fracture (*v. Boussingault*, C. R. 86, 1,303, and A. Ch. [5] 15, 91-126, and S. Kern, D. P. J. 231, 505).

An amalgam of chromium and *mercury* is produced by shaking up sodium amalgam in a solution of chloride or iodide of chromium. When the action ceases, the amalgam is heated with boiling water to remove the sodium. On heating the amalgam the mercury is volatilised, leaving the chromium as a sponge or powder.

*Detection of chromium.*—When heated strongly all compounds of chromium impart a green colour in both the reducing and oxidising flames to a borax bead. On ignition with potassium nitrate all chromium compounds produce a yellow colour due to the presence of potassium chromate. If this is dissolved in water, the addition of a solution of lead acetate produces a precipitate of chrome yellow.

Solutions of chromic salts or salts of sesquioxide of chromium have an acid reaction. With caustic alkalis they produce a green precipitate of hydrated oxide partially soluble in excess of the reagent, but reprecipitated on boiling the solution. With carbonates a green precipitate is produced, likewise soluble in excess.

Chromates (in which the chromium exists as an acid) are usually strongly coloured. Soluble chromates are reduced, when warmed with sulphuric acid and a reducing agent such as alcohol, with the production of a green colour. The chromium is then present as a base, and may be precipitated as already mentioned. When heated with hydrochloric acid they are also reduced with evolution of chlorine and formation of chromium chloride and chloride of the metal present as chromate.

Solutions of chromates, containing no free acid except acetic acid, give a yellow precipitate with a salt of lead, a red precipitate with silver nitrate, and a yellow precipitate with a salt of barium.

*Estimation.*—When present as a base, chromium is usually estimated as sesquioxide  $\text{Cr}_2\text{O}_3$ . For this purpose the solution is heated nearly to boiling, ammonia solution added in slight excess, and the temperature maintained until the liquid is perfectly colourless, indicating that the hydrate, which is slightly soluble in excess of ammonia, is completely precipitated. The precipitate is well washed by decantation and transferred to a filter, washed thoroughly with hot water, dried, and ignited. The oxide produced contains 68.43 p.c. of chromium. The precipitation is not complete in presence of organic matter, and when a

glass vessel is used, the precipitate always contains a small percentage of silica. Chromium, when present as a chromate, cannot be estimated directly by that method. It requires to be first reduced to a base. For this purpose hydrochloric acid and a small quantity of alcohol are added, and the solution heated until the odour of alcohol is dispelled. The chromium may then be precipitated as above. For the direct estimation of chromium in chromates, the precipitation with acetate of lead is most satisfactory. The solution is mixed with sodium acetate and acidulated strongly with acetic acid. A solution of normal lead acetate is then added, and the precipitate of  $PbCrO_4$  is collected on a weighed filter, washed, dried at  $100^\circ C.$ , and weighed. It contains 16.19 p.c. of chromium or 31.06 p.c. of chromic anhydride  $CrO_3$ . The following scheme may be adopted for the estimation of chromium in chrome iron ore. A few grams of the carefully sampled mineral are ground in an agate mortar and passed through a fine muslin sieve. The dust so produced is further ground in small portions until all grittiness on passing a little between the fingers has disappeared and the ore cakes as an impalpable powder round the pestle. About 0.5 gram of the powder is weighed into a platinum crucible of about 50 c.c. capacity, covered with twelve times its weight of recently fused hydrogen potassium sulphate (potassium bisulphate), and gently heated to just fuse the sulphate. After keeping at this temperature for fifteen or twenty minutes the heat is gradually increased until the crucible bottom becomes red-hot. The fused mass should not be allowed to rise above half way up the crucible. The mixture soon fuses quietly, and evolves dense fumes of sulphuric acid; the heat is gradually increased to bright redness. In about half an hour 6 parts of powdered anhydrous sodium carbonate are added and the mixture again fused for an hour at a red heat, 6 parts of nitre being added in small portions. The temperature is then raised to a full red heat for about twenty minutes; the crucible cooled and transferred to a porcelain basin where the mass is boiled out with water. The solution is filtered, and the residue washed with hot water until the filtrate comes through colourless. The filter and its contents are dried, the precipitate detached and placed with that still remaining in the basin, the filter paper burned, and the ash also added. To ascertain if the fusion has been satisfactory this residue is digested with moderately strong hydrochloric acid, when the whole should dissolve. Any insoluble black residue indicates either imperfect grinding or insufficient fusion. It must be collected on a filter, dried, and the whole ignited in a crucible and treated with potassium bisulphate  $K_2SO_4$ , as in the first instance. The aqueous extract after fusion is mixed with the main solution. To the liquid, a few grams of ammoniac nitrate are added, and the whole evaporated to dryness, taken up with water, and filtered from the alumina, silica, &c., into a porcelain basin. An excess of sulphurous acid solution is then added, and the solution heated until that gas is nearly expelled. The chromate having thus become reduced to chromium sulphate a slight excess of ammonia is added, and the solution boiled until

colourless. The precipitated chromium hydrate is washed by decantation with hot water, transferred to the filter and washed with hot water six times. The use of the suction pump will be of great assistance in this operation. The precipitate and filter are then dried, transferred to a weighed platinum crucible and heated gently until the paper is charred. The crucible lid is then placed at the edge of the crucible so that the flame may reverberate into the crucible, and the whole ignited strongly for ten or fifteen minutes. The weighed precipitate should show no yellowish colour on treatment with a few drops of water; if such a colour is produced it indicates imperfect washing of the precipitate from alkaline salts. The oxide contains 68.63 p.c. of chromium.

#### COMPOUNDS OF CHROMIUM.

Chromium forms five distinct oxides: chromous oxide  $CrO$ ; chromic oxide or sesquioxide  $Cr_2O_3$ ; chromic anhydride  $CrO_3$ ; an oxide  $CrO \cdot Cr_2O_3$  intermediate between the two first, corresponding to the magnetic oxide of iron; and  $Cr_2O_3 \cdot CrO_3$  or chromic chromate, which appears to be a combination of chromic anhydride and the sesquioxide. Three definite series of compounds are known, corresponding to the three first-mentioned oxides. (1) Chromous compounds, or salts of the protoxide. (2) Chromic compounds, or salts of the sesquioxide. (3) Chromates, in which the chromium acts as an acid. Of these, the chromous compounds are of no industrial importance.

**Chromic oxide** *Chromium sesquioxide*  $Cr_2O_3$ . This compound is produced by the oxidation of metallic chromium and by ignition of chromic anhydride and certain chromates.

Wöhler prepared this oxide in fine, small rhombohedral crystals by passing the vapour of chromyl dichloride through a tube heated to redness. The crystals are isomorphous with corundum and of equal hardness; their sp.gr. is 5.21. The finest coloured amorphous chromium oxide is produced by the ignition of mercurous chromate  $Hg_2CrO_4$  in a covered crucible; mercuric oxide and oxygen escape, and the oxide remains as a green powder. For the preparation of this substance on the large scale a great number of methods are recommended.

Boil a solution of potassium bichromate with half its weight of flowers of sulphur so long as the green hydrate is precipitated. The addition of a little potash solution, by forming potassium sulphide, accelerates the decomposition. The precipitate is filtered from the solution containing potassium sulphate and washed. The sulphur retained in the precipitate may be removed by gentle ignition. Instead of performing the reaction in the wet way, the mixture may be ignited in a crucible, and the resultant mass digested with water (Lassaigne, A. Ch. [3] 14, 299). In place of sulphur, Wöhler (P. A. 10, 46) mixes the bichromate with ammonium chloride, and treats as above.

According to Barian (Rev. Scient. 20, 425) a very pure colour, suitable for colouring fine porcelain, is produced by igniting in a crucible a mixture of 4 parts of potassium chromate and 1 part of starch. The mass is washed free from potassium carbonate and re-ignited.



Chromic sesquioxide is a green pigment of great permanence. It is not acted upon by chlorine or sulphur gases or by an intense heat. At a white heat it melts, and crystallises on cooling.

Hydrogen and carbon monoxide are without action, but it is reduced to the metallic state on intense ignition with carbon.

This oxide is largely used under the names *chrome green* and *ultramarine green* for imparting a green colour to glass, porcelain, &c. as a pigment, in oil and water colours and in printing, and as a mordant in calico printing and dyeing. Certain hydrated oxides are also used under various names; their colours are generally speaking brighter than that of the anhydrous oxide, but they usually contain small quantities of other substances besides the oxide and water.

*Guignet's Green*; *Pennettier's Green*; *Emerald Green*; *Veridian*  $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . This pigment appears to be identical with that formerly manufactured in secret by Pennettier. According to Guignet's method (Rep. C. P. A. 1859, 198) 3 parts of boric acid and 1 part of potassium bichromate are heated to dull redness in a reverberatory furnace. The mass swells up, evolves oxygen and becomes of a fine green colour; it contains the borates of potassium and chromium, or a double borate of those two metals. It is boiled with water, whereby the borate of chromium is decomposed into boric acid and hydrated chromium sesquioxide, potassium borate also remaining in solution. The precipitate is well washed, dried, and finely ground. It usually contains boric acid even after thorough washing. The washings and mother liquors are evaporated for the recovery of the boric acid.

According to the C. Z. 9, 851, the process now used on the large scale is as follows. The boric acid is first purified by solution in hot water, treated with animal charcoal, and recrystallised. The crystals are dried in a centrifugal machine. The mother liquor may be employed three or four times for recrystallisation of fresh portions of acid, but becomes then too impure for further use. Eight parts of the purified boric acid are mixed with 3 parts of potassium bichromate, all powdered, and 45 kilos. (100 lbs.) of the mixture heated to dull redness on the bed of a reverberatory furnace for about 4 hours. The fused mass is washed repeatedly by decantation and the residue placed on cotton filters, drained and passed through colour mills. After grinding it is again washed with hot water, filtered and pressed.

The two first washings are mixed and evaporated to 13° B. in leaden pans, treated with hydrochloric acid to convert the potassium borate into potassium chloride and boric acid, and the latter crystallised out. The mother liquors are evaporated to 20° B. and crystallised. The crystals are redissolved, treated with sulphuretted hydrogen to precipitate the lead which has been dissolved from the pans, filtered, and recrystallised. In this manner about 65 p.c. of the boric acid is recovered.

Guignet's green is unacted upon by light or concentrated boiling alkalis; hot hydrochloric acid slowly dissolves it. When heated to 200°C. it becomes anhydrous. It is a fine green pigment largely used for the same purposes as the

ordinary oxide. It may be used in place of the dangerous arsenical greens. When mixed with chromate of lead it is employed for the production of a pale green colour in landscape painting. The annual production is about 300,000 kilos. (294 tons).

*Arnaudon's Green*. A green pigment has been prepared by Arnaudon (Rep. C. A. 1859, 200) as follows. A mixture of 1 part of ammonium phosphate with rather more potassium bichromate is dissolved in the minimum of boiling water, and evaporated until the mass solidifies on cooling. It is then thrown in small pieces into a flat vessel and heated to about 180°C.; water and ammonia vapour are given off. After half an hour the temperature is raised to 200°C. for a short time. Too high a temperature injures the colour. The mass is well washed with hot water and the residue dried and powdered.

This pigment appears to consist mainly of a hydrated sesquioxide, but phosphoric acid is always present. It possesses a very fine colour, is permanent and non-poisonous. It is equal in appearance to Schweinfurth green and may replace that pigment with advantage.

According to Bong (B. 29, 201), a blue pigment, retaining its colour at high temperatures, suitable for colouring porcelain, &c. is produced by igniting strongly, in the air, an intimate mixture of 5 parts boric acid, 15 parts alumina, 20 parts magnesium carbonate, and 2 parts barium chromate.

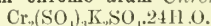
**Chromic chloride** or  $\text{CrCl}_3$  or  $\text{Cr}_2\text{Cl}_6$ . The anhydrous chloride is obtained by heating a mixture of carbon and chromium sesquioxide in a current of chlorine. It forms pale violet scales of sp.gr. 3.03, slowly soluble in hot water, readily soluble in presence of a trace of chromous, cuprous, or stannous salt. Chromic chloride may be prepared in solution by dissolving the hydrate in hydrochloric acid. It is deposited from solution by spontaneous evaporation, in crystals containing  $\text{Cr}_2\text{O}_3 \cdot 4\text{HCl} \cdot 10\text{H}_2\text{O}$  (Péligot). In calico-printing, a neutral solution of chromic chloride, prepared from potassium bichromate, is frequently used. The following method is recommended by De Karrer. Dissolve 9 lbs. of potassium bichromate in 5 gallons of boiling water. Prepare also a solution of 9 to 11 lbs. of white arsenic in 24 gallons of boiling water, and mix, with constant stirring, with the solution of bichromate. A greenish precipitate of chromic hydrate soon separates; it is cooled, filtered, and washed with boiling water. The precipitate is added in portions to a solution of hydrochloric acid (diluted until it no longer fumes), with constant stirring, until a portion remains undissolved. A solution of soda is then added and well mixed, until the hydrate begins to precipitate. The dark-green solution being thus neutralised is evaporated to 46° B. and is ready for use.

**Chromic fluoride**  $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ . This product is used in the printing and dyeing of woollen goods. It is a fine crystalline green powder, very soluble in water. In most cases it may be used in the place of acetate or nitrate of chromium for printing. Alizarin dyes, carulein, gallcin, &c. and logwood extracts, are fixed as perfectly as with acetate of chromium. One advantage in using it is that it is solid. For wool, 'fluorchrome' is a very good mordant,

since the fibre combines with the chromic oxide. Thus alizarin dyes and logwood dye wool mordanted with it very well (G. Stein, C. Z. R. 12, 91; S. C. I. 7, 385).

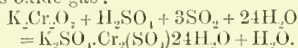
**Chromic sulphates.** Both basic normal and acid sulphates of chromium exist, but are of no commercial interest. The double sulphates of chromium and potassium, sodium and ammonium, are, however, of importance. These are known as *chrome alums*; they crystallise in fine octahedral crystals containing 24 molecules of water isomorphous with those of ordinary alum and of corresponding composition.

**Potassium chrome alum** *Chrome alum*



This substance may be prepared by mixing solutions of chromic sulphate and potassium sulphate in molecular proportions.

The best method is to add 5 parts of strong sulphuric acid to a solution of 3 parts potassium chromate in 30 parts of water with the addition of a reducing agent, preferably a current of sulphurous oxide gas:



When the sulphurous oxide is substituted by other reducing agents, such as alcohol, a larger quantity of sulphuric acid is required.

Chrome alum is obtained in large quantities as a by-product from the oxidation of organic substances, by a mixture of potassium bichromate and sulphuric acid, as in the oxidation of anthracene to alizarin, in the manufacture of aniline violet, &c.

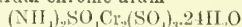
It crystallises in fine dark-purple octahedra, especially in presence of excess of acid, is soluble in 7 parts of cold water, forming a reddish blue solution, which when heated to about 70° becomes green. It returns to its original colour after standing some weeks.

When heated to 25–30°C. the crystals lose half their water and become lilac-coloured, at 100° a further quantity of water escapes and the crystals turn green; at 350° they become anhydrous, but are still soluble in water; at a temperature slightly above 350° they become greenish yellow, insoluble in water (Löwe) and only slowly soluble in acids.

Chrome alum is used in dyeing, calico printing, and tanning.

**Sodium chrome alum**  $\text{Na}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , corresponds to the potassium salt but is more soluble in water.

**Ammonium chrome alum**



is prepared like the preceding alums. It is less soluble in water than potassium chrome alum. It melts at 100°C.

**Chromium chlorate**  $\text{Cr}_2(\text{ClO}_3)_3$  is used to some extent in calico printing (Despieres and others, D. P. J. 228, 260–263). It may be prepared by the addition of a solution of potassium chlorate to chrome alum; the chromium then becomes converted into chromium chlorate and the potassium into sulphate. According to Lauber and Weinreb (D. P. J. 257, 290) it is best prepared by the following process. Dissolve 60 parts of chrome alum in 80 parts (by weight) of hot water; add 20 parts of soda dissolved in 60 parts of water, and wash the precipitated hydrate. Redissolve the precipitate in

10 parts of cold sulphuric acid of 66°B., filter if necessary and add 22 parts of potassium chlorate dissolved in 50 parts of water. The solution is evaporated slightly and the potassium sulphate crystallised out; the more soluble chlorate of chromium remains in solution.

**Chromic anhydride** *Chromic acid*  $\text{CrO}_3$ . This important oxide is best prepared by the decomposition of a chromate by sulphuric acid. A cold saturated solution of potassium chromate is added to from 1 to 1½ parts of concentrated sulphuric acid, with constant stirring. On cooling, if the acid used be strong enough, crimson crystals of chromic anhydride separate; if necessary the solution is evaporated until the crystals are formed on cooling. The liquid is poured off and the crystals drained on porous tiles or pressed between porous plates. They may be recrystallised by dissolving in water and evaporating to a syrup. The excess of sulphuric acid may be removed by the cautious addition of barium chromate to the solution of the crystals, or the crystals may be gently fused, when the heavier oxide sinks to the bottom of the vessel and the sulphuric acid above slowly evaporates. The motherliquors from the chromic anhydride are used for a fresh preparation until the percentage of potassium sulphate becomes excessive; they are then precipitated by the addition of lead acetate with the production of a light-coloured 'chrome yellow' containing much lead sulphate.

According to Zettnow (P. 143, 468) the largest yield is obtained as follows:—300 kilos. of potassium bichromate are dissolved in 500 c.c. of water and 400 c.c. of strong sulphuric acid are added. The mixture is allowed to stand for 10 or 12 hours, the solution decanted from the deposited crystals of potassium sulphate, and heated to 80° or 90°C.; 150 c.c. of sulphuric acid are then added, followed by sufficient water to redissolve the chromic anhydride at first deposited, and the solution evaporated until the oxide commences to crystallise. The mixture is allowed to stand for 12 hours, decanted from the crystals and evaporated with the production of a second and third crop of crystals. The crystals are drained, introduced into a crucible, mixed thoroughly with 50 c.c. of nitric acid of not less than 1·46 sp. gr. (weaker acid would dissolve the crystals) and drained for some hours on a tile. The operation is repeated if necessary with 25 c.c. of nitric acid. The whole of the sulphuric acid and sulphate having been thus removed, the crystals are heated on a sand bath and the nitric acid evaporated. In this manner Zettnow has obtained from 85 to 90 p.c. of the theoretical yield of *pure dry* chromic anhydride.

Duvilliers (C. R. 75, 711) prepares this oxide by dissolving 100 parts of barium chromate in 100 parts of water and 140 parts of nitric acid of sp. gr. 1·38 (10°B.) and heating the solution until it becomes red. 200 parts of water are then added and the whole boiled for 10 minutes; cooled, and the barium nitrate allowed to crystallise out. The solution is decanted, evaporated to the bulk occupied by the original amount of acid used, and a further crop of crystals of barium nitrate removed. The solution, which contains only about 1 part of barium nitrate for 200 parts of the anhydride, is evaporated nearly

to dryness, a little water added and the evaporation repeated until all the nitric acid is driven off. The anhydride is then crystallised out and dried as usual.

Barium chromate is digested for some time with about half the amount of dilute sulphuric acid required for complete precipitation with the production of chromic anhydride and barium bichromate and precipitation of barium sulphate. Sufficient sulphuric acid is then added to just precipitate the barium, and the solution, which only contains chromic anhydride, is decanted from the precipitate and the solution evaporated (Meissner). According to C. Watts the barium chromate is best treated with excess of strong nitric acid, the precipitated chromic oxide filtered through asbestos, and the nitric acid driven off by heat. Chromic anhydride is a powerfully acid substance crystallising in scarlet rhombic prismatic needles of sp. gr. 2.788 (Zettinow). They are stated to melt at  $192^{\circ}\text{C}$ . but remain liquid at  $172^{\circ}$ , the temperature rising to  $195^{\circ}\text{C}$ . when the mass solidifies.

When heated to  $250^{\circ}$  they decompose into the chromate of chromium  $\text{CrO}_3\cdot\text{Cr}_2\text{O}_3$  with evolution of oxygen. Above that temperature the whole is converted into chromium sesquioxide. By the action of light on a solution of this oxide, oxygen is evolved and the chromate of chromium precipitated as a brown powder.

Chromic anhydride is very soluble in water. 100 parts of water at  $26^{\circ}\text{C}$ . dissolve 62 parts of the oxide. It dissolves in acetic acid and ether without decomposition; is almost insoluble in sulphuric acid of 1.77 sp. gr. but dissolves in stronger or weaker acid; is insoluble in nitric acid of sp. gr. 1.46.

Chromic anhydride is a powerful oxidising agent. Warm anhydrous alcohol inflames when dropped upon it, and even dry ammonia gas is oxidised with production of water and nitrogen. A solution of the anhydride in acetic acid is largely used as an oxidising agent in organic work.

It has the property of producing a permanent yellow colour with silk or wool, but not with cotton. The chromium in such material may be converted into lead chromate upon the fibre or further dyed by logwood, &c. Chromic anhydride usually contains sulphuric acid and sulphates or nitrates; Moissan has found 24 p.c. of sulphuric acid in samples of the commercial article.

**Chromates.** *Chrome iron ore.* All chromates are prepared, directly or indirectly, by the action of oxidising agents upon *chrome iron ore* or *chromite*  $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ . This important mineral is found in a large number of localities, principally in Baltimore, Norway, and the Shetland Islands; also in Asia Minor, Siberia, and New South Wales. Large deposits of iron ore are found in New Caledonia containing sometimes 5 p.c. of chromium sesquioxide in a form soluble in acid, probably as chrome ochre.

Chromite belongs to the spinelle group of minerals. It is isomorphous with magnetic iron ore  $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ , and may be considered as that substance in which the sesquioxide of iron is replaced by sesquioxide of chromium; samples of some chromite are *magnetic*. A portion of the chromium is usually replaced by aluminium, and

some of the iron by magnesium, though this is sometimes absent. The composition of chromite varies extremely; an ore containing 50 p.c. of the sesquioxide is of very good quality. Of seven samples from varying localities analysed by Clouet, the chromium sesquioxide present averaged 44 p.c. A crystalline sample from Baltimore analysed by Abich showed  $\text{Cr}_2\text{O}_3$  60.04,  $\text{FeO}$  20.13,  $\text{Al}_2\text{O}_3$  11.85,  $\text{MgO}$  7.45.

Chromite is black or brownish-black, and infusible before the blowpipe. It will scratch glass, but is itself scratched by a good steel knife.

A scheme for the analysis of chromite has been given under the estimation of chromium.

**Potassium chromates.** Both the normal and acid chromates are of importance in the arts. The acid or bichromate, containing the larger proportions of the active constituent  $\text{CrO}_3$ , is generally prepared on the large scale.

A great number of processes have been adopted for the treatment of chromite for this purpose; they all depend upon the oxidation of the chromium sesquioxide into chromic anhydride.

The ore is heated to redness and plunged into cold water to facilitate the powdering, stamped, ground in a mill, and finely sifted.

In former times the ore was mixed with about two-fifths of its weight of potassium nitrate and ignited on the bed of a reverberatory furnace, the oxygen required for the oxidation of the sesquioxide into the anhydride and the potassium for its conversion into potassium chromate being both provided by the nitrate. A great saving was introduced by the substitution of atmospheric oxygen as the oxidising agent in place of the nitre, the potassium being supplied by potassium carbonate or, as proposed by Watt, by potassium sulphate. The mass, however, was very liable to fuse and the heavy particles of chromate to sink through the liquid and escape the action of the blast. This difficulty was overcome by Stromeyer, who introduced lime into the mixture, thus rendering the mass porous and non-fusible and much increasing the rapidity and completeness of the action.

Tilghmann (Patent 1847) makes use of felspar as the source of alkali. For this purpose 1 part of chrome ore is mixed with 4 parts of felspar and 4 parts of lime or 7 parts of chalk. The mixture is heated to bright redness, but not to fusion, in a reverberatory furnace for about twenty hours, with constant stirring. The chromate thus produced is removed as described later.

The ore may also be mixed with potassium chloride, and heated to whiteness with frequent stirring while a current of superheated steam is passed over the mass; the iron is stated to pass away almost entirely as chloride (Swindells, Ch. G. 1851, 419).

Jacquelain (A. Ch. [3] 21, 478) prefers to produce calcium chromate in the furnace and to convert it subsequently into the required chromate by double decomposition. He thus avoids the loss of alkali always experienced in the ordinary process. The ore is *finely powdered*, preferably levigated and dried before use, mixed ultimately with chalk in the required proportions and heated to bright redness on the bed of a re-



reverberatory furnace for nine or ten hours, with occasional stirring (at least once an hour). The product is ground in a mill, suspended in hot water, and treated with sulphuric acid until slightly acid; bichromate of calcium is thus produced. A little chalk is stirred into the solution to precipitate the iron as oxide, and a solution of potassium carbonate or other salt, according to the chromate required, is added. The calcium is thus precipitated as carbonate and the bichromate required remains in solution. The solution may also be used directly for the production of chrome yellow &c.

According to Booth's method (Pat. 1852) D. P. J. 131, 137) the ore is mixed with one-fifth of its weight of charcoal or coal and ignited in a reverberatory furnace like that used for puddling iron, out of contact with the air. The product is thrown into vats, and the reduced iron dissolved out by dilute sulphuric acid, the residue being treated in the usual manner for the production of chromates. The weight of oil of vitriol used amounts to about two-thirds that of the ore. It is stated that the value of the ferrous sulphate obtained repays the extra labour involved.

Acherley (Hoffman's Ber. ii. Entw. C. I. [1] 725) gives a description of the manufacture of potassium bichromate as usually practised on the large scale, of which the following is the abstract:—

The ore is stamped, ground in a mill, and passed through a sieve of eighty meshes to the inch.

Potash lye is prepared by soaking 7 cwt. of burned limestone (containing but little silica and magnesia) in a solution of  $2\frac{1}{2}$  p.e. of potassium carbonate free from chloride (which would hinder the crystallisation of the product), dried, ignited, and powdered.

It is then mixed with 4½ cwt. of the ore, and spread in a layer 2 inches deep upon the previously heated bed of a reverberatory furnace, at the end nearest the fire. The furnace is about 9 feet long and 6 feet broad. The heat is maintained at bright redness, and the mixture turned over every 15 minutes; in about 2 hours it is gradually pushed towards the farther end of the furnace, and its place supplied by a fresh charge. The operation is completed in about 4 hours, when the mass is greenish yellow and contains chromates of potassium and calcium, lime, potassium silicate, and ferric oxide. It is broken into coarse powder and lixiviated in wooden pans, placed steplike one above another, with a hot solution of potassium sulphate, which converts the calcium chromate into potassium chromate with precipitation of calcium sulphate. The liquid is allowed to run from one vat to another, until at last a saturated solution of potassium chromate is produced. This is run into a depositing vat lined with lead and treated with sufficient sulphuric acid and water to convert the normal salt into the bichromate, and the solution cooled.

As the solution of normal chromate was saturated and contained about 1 part of salt in 2 parts of solution, the bichromate solution formed is supersaturated, that salt requiring nearly five times as much water for solution as the normal chromate; about three-quarters of the

total amount in solution is thus deposited on cooling. The crystals are redissolved in sufficient water to form a solution of 1:120 sp.gr. and crystallised in deep iron pans at a temperature of 21°C.

Potassium chromate  $K_2CrO_4$  is prepared, as already described, from chrome ore. It may be produced by the addition of potassium hydrate to a solution of the bichromate. It crystallises in anhydrous yellow rhombic prisms isomorphous with those of potassium sulphate. 100 parts of water at 0°C. dissolve 59 parts of potassium chromate; at 100° 79 parts are dissolved. The solution has a fine yellow colour of great tinctorial power; a distinct yellow tinge is imparted by 1 part in 400,000 parts of water. It is insoluble in alcohol and ether, and is very poisonous. Its sp.gr. is 2.71 (Kopp).

When heated to redness with reducing agents, such as sulphur, it is reduced to chromium sesquioxide. The addition of an acid, even carbonic acid, determines the decomposition into bichromate of potassium. This change is not brought about by the less heat of formation of chromates than of salts of the decomposing acids, but by the greater heat of formation of bichromate than of chromate of potassium (Berthelot, C. R. 96, 399). According to Schwartz (D. P. J. 186, 31) the addition of the calculated quantity of sulphuric or other acid is not sufficient to produce the complete decomposition of normal into acid chromates; a considerable excess is required.

Potassium chromate is not largely used, the bichromate, on account of its greater richness in chromic acid, being generally preferred. The general uses and oxidising properties, however, described under bichromate of potassium, also apply to the normal chromate.

Potassium bichromate, generally known as 'Bichromate,' or 'Bichrome,'  $K_2Cr_2O_7$ . This important salt is prepared in large quantities by the methods already described. Considerably over 10,000 tons are annually produced in Great Britain.

It crystallises in anhydrous, fine, red, square tables derived from triclinic prisms of sp.gr. 2.692, and of intensely metallic, bitter taste. They melt at about 400°C. (Tilden and Shennstone), and resolidify on cooling without change. At bright redness decomposition ensues, and the normal chromate and chromic sesquioxide result.

100 parts of water at 0°C. dissolve 4.6 parts; at 20° 12.4, and at 100°C. 94.1 parts of the salt (Allnard, A. 133, 292).

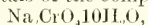
Potassium bichromate is used in the preparation of all chrome pigments; of 'discharge' for turkey red, &c.; for the production of a large variety of colours in calico-printing and dyeing; in the manufacture of safety matches, &c. In solution with sulphuric acid it is used as a bleaching agent for tallow, palm oil, &c.; in the oxidation of anthracene to alizarin, and in the manufacture of aniline violet. For the use of potassium bichromate in tanning leather *v. Donald* (S. C. I. 1884, 615). When mixed with organic substances it is reduced on exposure to light; gelatine under such circumstances is rendered insoluble. This reaction with gelatine is of great importance, and may be applied to

many purposes. It is taken advantage of in the 'Carbon' process of photography. The gelatine is mixed with a pigment of any colour, and the paper carrying this film is sensitised by floating on a solution of potassium bichromate. On exposure under a negative the gelatine in those portions exposed to the light becomes insoluble, and retains the pigment, while the portions protected by the darker parts of the negative are almost unacted upon, and may be dissolved in warm water. In this manner photographs of any desired colour, and of great beauty and permanence, may be produced; but in the actual process a large number of details require attention, rendering the method somewhat difficult.

**Sodium chromates.** The normal chromate  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  and the bichromate  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  are prepared by methods corresponding to those used for the potassium salts. According to Nac. Walberg (D. P. J. 259, 188) they are prepared on the large scale as follows; 6 parts of powdered chrome ore (41 p.c.  $\text{Cr}_2\text{O}_3$ ) are mixed with 3 parts soda ash (92 p.c.  $\text{Na}_2\text{CO}_3$ ) and 3 parts of chalk, and heated in charges of 1 ton in a reverberatory furnace for eight hours. The mass is lixiviated to produce a solution of  $45^\circ\text{B.}$ , boiled down to  $52^\circ\text{B.}$ , and allowed to crystallise in leaden pans. The crystals are first dried by a centrifugal machine, and finally heated to  $30^\circ\text{C.}$  in a drying chamber, where they crumble to a yellow anhydrous powder containing about 96 p.c. of the normal chromate.

For the production of bichromate these crystals are dissolved to a solution of  $40^\circ\text{B.}$  and treated with sufficient chamber acid to determine the conversion into the bichromate, the right point being found by potassic iodide and starch paper. Sufficient neutral sodium chromate is then added to bring the percentage of  $\text{Cr}_2\text{O}_3$  to about 72.5. The liquor is cooled in lead tanks to  $1^\circ\text{C.}$ , artificially if necessary, and the sodium sulphate crystallised out. The liquor is drained off, filtered if necessary, and evaporated to dryness in an iron pot, with constant stirring. The residue is powdered while still hot. If the amount of  $\text{Cr}_2\text{O}_3$  be allowed to exceed 72.5 p.c., the product is damp and cannot be stored in wooden casks. An analysis of this substance showed  $\text{Cr}_2\text{O}_3$  72.3,  $\text{Na}_2\text{O}$  26.20,  $\text{SO}_3$  1.40.

*Normal chromate of sodium* forms fine large efflorescent crystals of the composition



isomorphous with Glauber's salt. Unlike the chromate of potassium, it is less soluble than the bichromate.

*Bichromate of sodium*  $\text{K}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  crystallises in thin, six-sided prisms with bevelled edges of a fine hyacinth-red colour, and is very soluble in water.

The *chromate* and *bichromate of ammonia* are prepared by mixing in proper proportions solutions of ammonia and of chromic acid.

**Lead chromates.** The *neutral chromate of lead*  $\text{PbCrO}_4$  is best produced by the action of a solution of lead acetate on a solution of a chromate. Thus produced, it is of a fine lemon-yellow colour, insoluble in water and dilute acids. When heated to  $250^\circ\text{C.}$  it becomes a reddish brown, at a higher temperature it fuses, and finally evolves oxygen with the formation of chromic sesquioxide and a basic lead chromate.

On account of this evolution of oxygen on heating, this substance is frequently used in organic analysis.

Lead chromate is soluble in cold lime water or caustic alkali, but is unattacked by hot lime water. For this reason, in immersing calico coloured with chrome yellow in lime water, for the production of an orange colour, care should be taken that the solution is hot.

When heated with caustic alkali a portion of the chromic oxide is removed, with the production of a basic lead chromate of colour varying from orange to vermillion.

The *normal chromate* is largely used as a pigment, and for calico printing, &c., as *Chrome Yellow*, *Paris Yellow*, *Leipsic Yellow*; when mixed with baryta or other substance to lower the colour, as *Cologne Yellow*, and, when mixed with Prussian blue, as *Green Cinnabar*.

The *basic chromate* is used under the names *Chrome Red*, *Austrian Cinnabar*, *Persian Red*.

By an appropriate mixture of the normal and basic chromates, or by differences in the preparation, any shade between lemon-yellow and vermillion may be produced. Such colours are known as *Chrome Orange*. Many methods are in use for the preparation of these pigments. The finest chrome yellow is produced by precipitation; the lead acetate used should not be basic, or the product will be of an orange colour; the solution should be dilute, and the lead salt should be in excess; the presence of excess of chromate is liable to 'turn' the yellow—i.e. to produce an orange tint. The substances used should be comparatively pure.

For the lighter or 'Cologne yellow' the solution of chromate is mixed with an appropriate quantity of alum or of sulphuric acid before precipitation. The lead chromate is thus precipitated, together with any desired amount of sulphate, and the colour correspondingly lowered. The bichromate solution may also have baryta, gypsum, or kaolin stirred in before the addition of the lead. Bouthron Chatard gives the composition of ordinary Cologne yellow as  $\text{CaSO}_4$  60 p.c.,  $\text{PbSO}_4$  15 p.c.,  $\text{PbCrO}_4$  25 p.c.

Biot and Delisse first precipitate lead sulphate from a solution of the acetate, and digest 3 parts of the washed precipitate with 1 part of normal potassium chromate dissolved in hot water. The chromate is thus wholly converted into chrome yellow, mixed, or perhaps combined with the lead sulphate, and a 'Cologne yellow' of good colour is produced. The colour is said to be equal to that obtained when double the quantity of chromate has been used. Its covering power is, however, stated to be inferior to that of the precipitated yellow.

Liebig uses for this purpose the sulphate of lead obtained in dye-works &c. as a by-product. The pigment, on account of the basic character of the sulphate, is of an orange colour.

Anthon substitutes lead chloride for sulphate, treating 100 parts of freshly precipitated chloride with 27 parts of bichromate.

Runge mixes 45 parts of litharge, 6 parts of salt, and 50 parts of water; the mass becomes white, and swells considerably; more water is added to prevent it from hardening. In three or four days the whole has been converted into lead oxychloride; a solution of 15 parts of po-

tassium bichromate is then poured on, and the mass well stirred and washed. A corresponding process is used with carbonate of lead, the colour produced being preferable to that when chloride, sulphate, or oxide of lead are used.

According to the Textile Colourist, the method generally adopted for the preparation of chrome yellow is as follows. For the preparation of the lead acetate four wooden tubs, 3 feet in diameter and  $1\frac{1}{2}$  feet high, are arranged one above another, so that the liquid may pass downwards from one to the other. They are filled with granulated lead, and strong wood vinegar poured on the uppermost; after remaining there for a few minutes it is run into the second, third, and fourth for an equal time. The surface of the lead is thus thoroughly acted upon, and becomes heated and oxidised by the air. The vinegar is then passed through a second time, remaining in each tub for an hour; on leaving the fourth tub a saturated solution of acetate is produced.

Bichrome is dissolved in 10 or 12 parts of water in steam-cased copper pans, and sufficient acetate added to just precipitate the chromate completely. The precipitate is settled, washed by decantation, filtered, and dried slowly on boards. The filtration should be performed as rapidly as possible because the pigment swells considerably while drying, and this should take place on the boards.

By mixing some chromate of lead with the lead acetate solution a dark lemon colour is produced, and by the addition of caustic potash to the precipitate a much redder pigment may be obtained.

For the production of a fine vermilion pigment Liebig and Wohler's method may be used. A mixture of equal parts of potassium and sodium nitrates is just heated to fusion, and chrome yellow, in small fragments, is dropped in; ebullition takes place and the mass becomes black. The heating should be continued until ebullition ceases. The chrome yellow has then become converted into basic chromate of lead and potassium chromate. If the temperature used be too high the product becomes brown and is spoiled. The supernatant yellow liquid is poured from the heavy basic lead salt, which is then well washed in water. The washings should be poured off as quickly as possible, or the action is liable to be reversed and the normal chromate reproduced in part, with a corresponding reduction of colour.

The red chromate may also be produced by boiling chrome yellow with half an equivalent of lime or of caustic alkali, or by the addition to a solution of lead acetate of potassium chromate to which an equivalent of potassium hydrate has been added.

For the production of a fine 'Persian red' Prinvtol digests 25 parts of lead carbonate in a cold solution of 10 parts of potassium chromate for 2 days. A red crystalline precipitate of basic lead chromate is thus produced, while potassium bicarbonate remains in solution. The mixture is boiled for half an hour, whereby a portion of the red precipitate becomes decomposed with the formation of normal lead chromate and of potassium chromate, turning a violet-red colour. This is filtered off, washed, and digested with

one part of sulphuric acid dissolved in 100 parts of water, with the production of 'Persian red.'

The colour of the varieties of chrome red is due principally to the size of the crystals, those pigments of which the crystals are largest being of the most intense colour.

**Calcium chromate**  $\text{CaCrO}_4 \cdot 4\text{H}_2\text{O}$  is largely produced in the manufacture of chromates from chrome iron ore. It is soluble in water and alcohol. It becomes anhydrous at  $200^\circ\text{C}$ , and, being then almost insoluble in water, is used as a pigment. It has a fine straw colour, and is used for distemper work; is permanent, but of slight covering power.

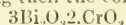
A bichromate of calcium is known, containing  $\text{CaCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ .

**Barium chromate**  $\text{BaCrO}_4$  is a canary yellow powder, known as *Yellow Ultramarine* or *Lemon Yellow*. It is produced by the addition of a chromate to a solution of a salt of barium.

Barium chromate is insoluble in water and acetic acid, soluble in hydrochloric and nitric acids. On treatment with a boiling solution of chromium anhydride it dissolves, and crystallises on cooling as a yellowish-red powder, consisting of the bichromate  $\text{BaCr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ .

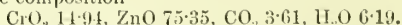
Barium chromate is used as a pigment; it is stated to become greenish on exposure to light.

**Bismuth chromates.** On the addition of potassium bichromate to a neutral solution of bismuth nitrate a yellow flocculent precipitate, soluble in acids, is produced, which becomes crystalline, having then the composition



(Löwe). On heating it becomes partly decomposed and turns greenish. From an acid solution of bismuth nitrate the precipitate formed consists of  $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$  (Löwe; Muir), and is quite insoluble in water. Bismuth chromate is used as a pigment and in calico-printing.

**Zinc chromate, Zinc Yellow, or Buttercup Yellow**  $\text{ZnCrO}_4$ , is a beautiful, stable, yellow pigment, produced by the addition of hot neutral solution of zinc sulphate to potassium chromate. According to Wagner, English-zinc yellow has the composition



**CHROMOMETERS** v. COLORIMETERS.

**CHRYSAMIN** v. AZO-COLOURING MATTERS.

Chrysamin not only dyes cotton without a mordant, but may, according to Knecht, even serve as a mordant for methylene blue, safranine, and aniline green. Galland has used chrysamin and similar colours, such as benzopurpurin and azo-blue, as mordants for various dyes, with the following results. Two minutes' immersion in a bath containing 1 gram chrysamin, 2.5 litres water, and 25 grams sodium phosphate for each square metre of the fabric, gave a canary-yellow shade. The best results were obtained with triphenylcarbinol derivatives, particularly with Victoria blue, its dark-blue shades resisting better than the others a soap bath for  $1\frac{1}{2}$  hours at  $70^\circ\text{C}$ . The shades obtained with aniline violet do not resist a soap bath so well, and if produced by magenta, methylene blue, malachite green, Bismarck brown, or safranine, they are entirely decomposed by a soap bath at  $70^\circ$ . Other colours, such as Coupler's grey, the phthalcin derivatives—cosin, erythro-



sin, cœrulein; anthraquinone derivatives—alizarin blue and the natural colours, logwood, Lima extract, cochineal, &c., are not fixed so well, or not at all, and are all entirely destroyed by soap. Benzo-purpurin and azo-blue behave towards aniline and anthracene colours, as also to the natural colours, like chrysamin, but the shades produced by the latter are faster (S. C. I. 5, 532).

**CHRYSANILINE** *Diamidophenylacridine*  $C_{18}H_{11}N_3$  is obtained as a by-product in the manufacture of rosaniline by the arsenic acid method, and was isolated by Nicholson (D. P. J. 168, 133) by treating the residue with steam, whereby chrys-aniline passes into solution and can be precipitated therefrom by addition of nitric acid. It was further examined by Hofmann (B. 2, 378), who prepared its methyl-, ethyl-, and phenyl-derivatives. Its composition and constitution were first established by Fischer and Körner (B. 17, 203; A. 226, 175; compare also Anschütz, B. 17, 433), who refer its formation in the rosaniline melt to a condensation and subsequent oxidation of orthotoluidine and aniline, since they have effected its synthesis by heating with arsenic acid at  $180^{\circ}$ – $200^{\circ}$  the orthodiparatriamidtriphenylmethane obtained by Renouf (B. 16, 1304) by the action of dehydrating agents on a mixture of orthonitrobenzaldehyde and aniline.

*Properties.*—Chrysianiline crystallises with 2 mol. of  $H_2O$  from 50 p.c. alcohol in golden-yellow needles, and from benzene with 1 mol. of benzene of crystallisation in golden-yellow scales; the latter melt when placed in a bath heated at  $150^{\circ}$ – $160^{\circ}$ , but when slowly heated lose the associated benzene, and melt, like the former, at  $267^{\circ}$ – $270^{\circ}$ . It is insoluble in water, and sparingly soluble in alcohol. On oxidation with chromic acid it yields acridine (A.), and when diazotised is converted into phenylacridine (m.p. =  $164^{\circ}$ ). *Chrysophenol*  $C_{18}H_{11}NO$ , a yellow dye, is obtained when it is heated at  $160^{\circ}$ – $180^{\circ}$  with concentrated hydrochloric acid, and crystallises from dilute alcohol with 2 mols. of  $H_2O$  in ruby-red needles. Chrysianiline forms two series of salts; of these the sparingly soluble nitrate is the most characteristic: it crystallises in ruby-red needles, and is employed under the name phosphine as a valuable golden-yellow dye for silk and wool.

**CHRYSAROBIN**  $C_{20}H_{12}O_7$ . This substance is a constituent, to the extent of 84 p.c. (Attfield), of araroba or Goa powder, the pith of a tree belonging to a species of *Casalpinia* (Holmes, Ph. [3] 5, 801), and was first extracted therefrom by Attfield (Ph. [3] 5, 721), who believed it to be chrysophanic acid, into which, indeed, it is readily converted on oxidation (Liebermann and Seidler, A. 212, 36). Chrysarobin is extracted from Goa powder by hot benzene, and when crystallised from glacial acetic acid forms small yellow laminae. It can be repeatedly crystallised without alteration, but is oxidised to chrysophanic acid when air is passed through its solution in aqueous caustic potash. It is distinguished from chrysophanic acid by dissolving in concentrated sulphuric acid with a yellow, and in concentrated aqueous caustic potash with a dark-green colour, whilst dilute aqueous potash does not dissolve it; chrysophanic acid, on the

contrary, yields a red solution with concentrated sulphuric acid and dilute aqueous potash (Liebermann and Seidler, B. 11, 1603) v. ARAROA POWDER.

**CHRYSAZIN** v. ALIZARIN AND ALLIED COLOURING MATTERS.

**CHRYSEINIC ACID** v. NAPHTHALENE.

**CHRYSENE**  $C_{18}H_{12}$  or  $\left< \begin{smallmatrix} C_{10}H_8 \cdot CH \\ C_{10}H_8 \cdot CH \end{smallmatrix} \right>$

This hydrocarbon occurs in the highest boiling portions of coal tar, and in the tarry products obtained in the dry distillation of wood, fats, and oils (Laurent, A. Ch. [2] 66, 136). Synthetically, it can be prepared by passing the vapour of benzylnaphthylmethane through a red-hot tube (Graebe and Bungener, B. 12, 1078).

*Purification.*—Chrysene is extracted from the mixture of solid hydrocarbons consisting chiefly of pyrene and chrysene, which boil at a higher temperature than anthracene and constitute the last portions of the distillate from coal tar, by repeated digestion with carbon bisulphide in the cold. This treatment removes all the hydrocarbons present in the mixture except chrysene (present to the extent of 18 to 19 p.c.), and this is further purified by crystallisation from coal oil (boiling point =  $150^{\circ}$ ), from which it separates in golden-yellow scales. The yellow colour, due to an impurity, cannot be removed by repeated crystallisation, but is destroyed by boiling with alcohol and a small quantity of nitric acid (Liebermann, 158, 299).

A second method for obtaining chrysene from crude greenish-yellow anthracene (m.p. =  $207^{\circ}$ – $208^{\circ}$ ) has been described by Schmidt (J. pr. [2] 9, 250, 270). For this purpose 40–50 grams of the anthracene are dissolved in 5 litres of strong (95 p.c.) alcohol, and the solution after filtration is boiled with 30 grams of nitric acid (sp.gr. = 1.4) in a reflux apparatus for some time. On cooling red needles of a sparingly soluble compound of chrysene and dinitroanthraquinone  $C_{18}H_{12} \cdot C_{14}H_8(NO_2)_2 \cdot O_2$  separate out, which when treated with tin and hydrochloric acid decompose into chrysene and reduction compounds of dinitroanthraquinone. The hydrocarbon is then obtained pure and colourless by crystallisation from benzene.

*Properties.*—Chrysene crystallises in scales, or in well-defined, colourless rhombic plates, melts at  $250^{\circ}$  and boils at  $436^{\circ}$ . It is a sparingly soluble substance; for example, 100 parts of absolute alcohol dissolve 0.097 parts at  $16^{\circ}$ , and 0.17 parts at  $18^{\circ}$ , and 100 parts of toluene dissolve 0.24 parts at  $18^{\circ}$ , and 5.39 parts at  $100^{\circ}$  (v. Bechi, B. 12, 1978), whilst ether, carbon bisulphide, benzene, and acetic acid dissolve it only to a slight extent at the ordinary temperature, but more readily on boiling. The solutions, like the pure hydrocarbon, show a deep reddish-violet fluorescence. Chrysene combines with dinitroanthraquinone and with picric acid (trinitrophenol) to form characteristic compounds; the *picrate*  $C_{18}H_{12} \cdot C_6H_2(NO_2)_3 \cdot OH$  obtained by adding chrysene to picric acid in benzene solution crystallises in long red needles and is decomposed by alcohol (Liebermann, Schmidt). When heated with concentrated sulphuric acid chrysene yields a sulphonic acid, and when treated with nitric acid under varying conditions yields mono-, di-, and tetra- nitro-

derivatives (*ibid.*), whilst chlorine and bromine convert it into substitution-derivatives (Schmidt). On oxidation with chromic acid in acetic acid solution, chrysene is converted into *chrysoquinone*  $C_{18}H_{10}O_2$ , which crystallises in yellowish red needles, melts at  $235^\circ$ , yields azines on treatment with ortho-diamines (Liebermann and Witt, B. 20, 2242), and is characterised by dissolving in concentrated sulphuric acid with a blue colour.

**CHRYSEOLIN** *v.* AZO-COLOURING MATTERS.

**CHRYSOBERYL**. *Beryllium aluminate v. ALUMINIUM.*

**CHRYSOCOLLA**. The Greek name for borax. Now applied to copper silicate *v.* COPPER.

**CHRYSOGEN**. An orange-coloured substance, containing more than 94 p.c. of carbon, and said to be a hydrocarbon, discovered by Fritzsche (Z. 1866, 139) in erude anthracene. It is sparingly soluble in the ordinary organic solvents. In sunlight its solutions become rapidly bleached, and yield a colourless crystalline compound which on fusion becomes orange-yellow.

**CHRYSOÏDINE** *v.* AZO-COLOURING MATTERS.

**CHRYSOÏN** *v.* AZO-COLOURING MATTERS.

**CHRYSOLINE** *v.* AZO-COLOURING MATTERS.

**CHRYSONAPHTHAZINE** *v.* AZINES.

**CHRYSOPHANIC ACID**  $C_{15}H_{10}O_4$  (De la Rue and Müller, C. J. 10, 298; Thann, A. 107, 324). This acid occurs in the roots of various species of *Rheum* and *Rumex* (H. Grothe, P. 113, 190). It can be obtained from rhubarb root, in which it occurs together with emodin, by extraction with benzene. After removal of the benzene by distillation, the residue is treated with aqueous caustic soda whereby emodin and other impurities are removed whilst the acid remains undissolved (Liebermann and Fischer, 183, 158). Chrysophanic acid may also be obtained from chrysarobin by oxidation with air in alkaline solution; the acid is then precipitated by the addition of a mineral acid, and crystallised from petroleum spirit (Liebermann and Seidler, B. 11, 1603).

Chrysophanic acid crystallises from alcohol in golden-yellow needles, and melts at  $162^\circ$ . It dissolves in 1125 parts of alcohol (86 p.c.) at  $30^\circ$ , and in 224 parts at the boiling-point, and is soluble in hot benzene, acetic acid, and amyl alcohol. When heated with zinc-dust it yields methylanthracene. Concentrated sulphuric acid and aqueous alkalis dissolve it, forming red solutions. (*V.* also CASCARA SAGRADA.)

**CHRYSOPHANIN** *v.* SENNA LEAVES.

**CHRYSOPHENIN** *v.* AZO-COLOURING MATTERS.

**CHRYSORETIN** *v.* SENNA LEAVES.

**CHRYSOTOLUAZINE** *v.* AZINES.

**CHRYSOTOLUIDINE**  $C_{21}H_{21}N_3$ . A yellow crystalline base of unknown constitution (*cf.* Hofmann, B. 2, 386) occurring in the residue obtained in fuchsin manufacture by the arsenic acid method (Girard, De Laire, and Chapoteaud (C. R. 63, 964; 64, 416). The hydrochloride is a yellow dyestuff.

**CIDER**, or **CYDER**, is a beverage produced by the fermentation of the juice of apples, and is

made in several counties of England, in Normandy, Holland, portions of Germany, and of the United States of America.

The best apples for the purpose are rather tough, piquant, and astringent. The kinds preferred are, in Devonshire, the Foxwhelp, Royal Wilding, Skrymc's Kernel, White Normandy Beech, and Yellow Styre; in Herefordshire, varieties of the Foxwhelp, known as the New, Old, Bastard, Red and Black Foxwhelp, Dymock Red, White Musk, Norman Cider, and others; in America the Harrison, the Red Streak, and the Virginia Crab. The apples now used for making the best qualities of cider are especial varieties, and are not suited for any other purpose. The kinds are roughly distinguished as 'early' and 'late,' according to the period of their maturity, so that by a judicious assortment in the orchards, the mill may be almost constantly kept at work. The soil in which the trees are grown should be strong and rich in phosphates, and should be systematically manured to ensure continuous heavy bearing. For this purpose a compost is recommended consisting of bone-dust 1 part, pure dissolved bone 1 part, kainit 2 parts, eharc coal-dust 20 parts.

The fruit having been gathered at the period of maturity, is placed in heaps until it becomes sufficiently ripe and mellow to be crushed; by this means an equal degree of ripeness is attained. Wherever possible the fruit should be kept under cover, since exposure to rain washes away a large proportion of those forms of torule occurring naturally on all kinds of fruit, and so essential to carrying on the process of fermentation. A certain proportion of the sugar is also liable to be carried away by rain.

Of course it is possible to make good cider from only one kind of fruit, but a mixture of different varieties of sweet and bitter-sweet gives more satisfactory results. All the fruit should be sound, for it is fatal to the manufacture of the finest cider that apples in every variety of condition should be promiscuously mingled. As an early writer says: 'This error or neglect hath not only been the occasion of much thin, raw, phlegmatical, soure, and unwholesome cider, but hath cast a reflection on the good report that cider, well made, most richly deserves.'

The methods employed in extracting the juice were until recent years of a primitive character. Mashing in a trough with pestles wielded by hand was the usual practice, or the fruit was thrown into a stone trough studded with nails, in which a cylinder of wood or stone similarly spiked was made to revolve by the aid of one or two horses. This form of mill still exists in many places. Where large quantities of fruit have to be dealt with, it is passed between rollers of wood or stone, exerting not only a pressing, but also a tearing action upon it. Some makers have designed these machines so as to disintegrate the pulp without bruising the seeds, under the belief that the flavour of the pips injures that of the cider. In grinding it is customary to sprinkle a little water over the apples, and, as the pulp is removed from the machine, to place it in wicker mats or in bags of hair-cloth, in which the juice is expressed from it. Sometimes water is

added to the solid portion remaining after the first expression, from which an inferior quality of cider results; occasionally even a third variety is made by again soaking and pressing the 'cake' or 'cheese.' Finally the residue is mixed with chaff and given to the cattle, or dried to form fuel, or thrown to the manure heap, thence to be returned to the orchard.

The prevalent practice in England is to remove the pulp or 'pommage' at once from the mill and to proceed to the pressing without delay. In America, however, it is customary to allow the pommage to stand in open vats for 24 to 48 hours or longer, whilst in Germany and in some parts of Normandy, it is left for from 5 to 12 days until fermentation is well established. It is claimed that by this delay the flavour, perfume, and colour of the fruit is conveyed to the liquor and to the resultant cider. As in the case of the pulping mill, the apparatus for pressing has been much improved of late years, the aim being to secure a gradual and not too forcible pressure. As it proceeds, the liquor, at first turbid, becomes later quite clear. The juice is placed in hogsheads of 50 gallons in Devonshire or of twice that capacity in Herefordshire, and fermentation rapidly sets in.

The process of fermentation should be carried on at a moderately low temperature if possible, never exceeding 10°F. Under favourable conditions, at this temperature the sugar is rapidly converted into alcohol and carbonic acid, large volumes of gas being given off, whilst at the same time a strong frothy head is thrown up. This consists principally of the lighter portions of tissue and other particles which have been pushed to the surface by the rising bubbles of gas. As soon as a certain proportion of alcohol is produced the fermentation becomes less active, the greater portion of matters in suspension begins to subside, and the liquid becomes moderately clear. At this stage it is racked off quickly into fresh casks where the secondary fermentation is carried on at as low a temperature as possible. The alcohol produced in the primary fermentation now acts in a very beneficial way, for where a normal quantity is present, not only does it serve to hold in check, or possibly prevent altogether, the development of organisms tending to produce acetous or possibly lactic fermentation, but it also takes up and helps to hold in solution the essential oils of the pips and skins of the fruit, which during the grinding and pressing had been released from the ruptured cells which contained them. By this means the cider acquires a delicious fruity aroma eminently characteristic of pure unsophisticated cider.

If, however, the apple juice, or must, be deficient in sugar, so that but little alcohol is produced and all the available sugar is used up in the primary fermentation, then after racking a certain amount of flatness ensues in the liquor and a great tendency to acetous fermentation is developed, so that in a short time we have a liquid consisting practically of a mixture of acetic acid with the malic acid originally present, and possessing a sourness more intense than vinegar. Under such circumstances it is advisable to add invert sugar to the pressed

must in such proportions as to bring the total quantity of sugar up to the normal.

Up to the present time little or nothing is known with regard to the species of yeast which carry on the process of fermentation of cider, but undoubtedly some one or more of the different varieties of *Saccharomyces Pastorianus* as well as *S. ellipsoideus* and *S. apiculatus* contribute largely to this, and it is extremely probable that a careful study of the yeast produced during cider fermentation, and a judicious selection of certain forms or types of cells for carrying on the various stages of fermentation, would result in the production of a liquor far superior to that which is at present known as cider, and calculated to take a very high rank among fermented beverages.

The strongest and best cider will keep in cask for 4 or 5 years, but the present custom is to bottle it in the spring following the autumn in which it has been made; by this means a much greater richness is obtained.

The following table represents the mean of many analyses of fresh apple-juice from the best fruit:

Water	800.00
Sugar capable of being converted into alcohol	173.00
Tannic acid or tannin	5.00
Mucilage or pectosine (soluble pectin, gum)	12.00
Free acids (malic, tartaric, &c.)	1.07
Albumen and fermentable matter	5.00
Saline matters (lime, malates of potash and of lime, phosphate of lime)	1.75
Pectic acid, colouring matter, fixed acid, volatile oils, and insoluble substances in suspension	2.18
	<hr/> 1000.00

The best and soundest cider should contain from 8 to 10 p.c. of alcohol (Hogg), with from 2 to 3 p.c. of sugar. The presence of a considerable amount of tannin and tannic acid causes the albumen and pectin to be deposited, thus fining the liquor; it regulates fermentation and prevents ropiness. Hence it is the custom with some cider makers to add a small quantity of good fresh hops to the must either before or after the primary fermentation has set in.

Another constituent of apple-juice is malic acid, and what tartaric acid is to the grape malic acid is to the fruit of our English gardens. But there the comparison ends, for whereas when grape-juice begins to ferment, directly an appreciable quantity of alcohol is formed, the tartaric acid begins to be thrown out of solution in the form of *argol*, and this process of elimination of the acid from the wine goes on as long as additional quantities of alcohol are formed. Now, if we could by any means manage to get rid of the malic acid in cider under somewhat similar conditions, a natural apple-wine of high-class merit might be manufactured in this and other apple-growing countries and which might very favourably compete with many of the grape-wines at present in the market.

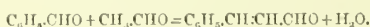
Cider, by careful manipulation, can be made to contain a very high percentage of spirit, ligar



and clean in character, free from fusel oil and rich in compound ethers, of fragrant aroma and delicate flavour, which when carefully distilled is capable of becoming a first-class brandy.

- CINCHAMIDINE** *v.* VEGETO-ALKALOIDS.  
**CINCHONAMINE** *v.* VEGETO-ALKALOIDS.  
**CINCHONIBINE** *v.* VEGETO-ALKALOIDS.  
**CINCHONIDINE** *v.* VEGETO-ALKALOIDS.  
**CINCHOMERIC ACID** *v.* BONE OIL.  
**CINCHONINE** *v.* VEGETO-ALKALOIDS.  
**CINEOL** *v.* CAMPHORS; SANTONICA.  
**CINNABAR**. *Mercuric sulphide, Vermilion,*  
*v.* MERCURY; PIGMENTS.  
**CINNABAR, GREEN,** *v.* CHROMIUM.  
**CINNAMEIN** *v.* Balsam of Peru, art.  
 BALSAMS.

**CINNAMALDEHYDE** *Cinnamic aldehyde*  
 $C_6H_5.CH:CH.CHO$  is contained, together with a hydrocarbon, in oil of cinnamon and oil of cassia. It may be extracted from oil of cinnamon by shaking the oil with a concentrated solution of sodium bisulphite, filtering off the crystalline bisulphite-compound, washing the latter with alcohol and distilling it with dilute sulphuric acid, when the cinnamaldehyde passes over with the steam. The cinnamaldehyde is extracted from the aqueous distillate with ether, and after expelling the ether, is purified by distillation under a pressure of from 40 to 50 mm. (Peine, B. 17, 2109). It is best obtained by allowing a mixture of 10 parts of benzaldehyde, 15 of ordinary aldehyde, 900 of water, and 10 of a 10 p.c. solution of caustic soda to stand at a temperature of about 30° for from 8 to 10 days, shaking from time to time:



The solution is extracted with ether and the ethereal extract treated as in the foregoing method (Krszysica, B. 17, 2117). Also formed when a mixture of calcium cinnamate and calcium formate is distilled (Piria, A. 100, 105).

It is a colourless oil with a pleasant aromatic smell of cinnamon. It decomposes when distilled under ordinary pressures, especially with access of air, but may be distilled without decomposition in a current of steam or under reduced pressure. It boils at 120-130° under a pressure of 20 mm. (Peine, B. 17, 2110). Sp-gr. 1.0497<sup>20</sup> (Brühl, A. 235, 18).

By oxidation it yields first cinnamic acid and afterwards benzaldehyde and benzoic acid. It gives the usual reactions of the aldehydes.

F. R. J.

**CINNAMIC ACID**  $C_6H_5.CH:CH.COOH$ . (*Acide cinnamique*, Fr.; *Zimmtsäure*, Ger.) The separation of a solid acid from oil of cinnamon on keeping was first observed towards the end of last century, but the acid was confounded with benzoic acid, until Bizio, in 1826, showed that it was a distinct acid. It was first thoroughly investigated by Dumas and Peligot (A. 14, 56).

*Occurrence*.—In liquid storax, partly free, partly as cinnamyl cinnamate (styracine); in tolu and Peru balsams together with benzoic acid and benzyl cinnamate; in some sorts of gum benzoïn; and in the leaves and stalks of *Globularia Alypum* and *G. vulgaris*, and in the leaves of *Enkianthus japonicus*.

*Formation and Preparation*.—It is formed by heating benzaldehyde with acetyl chloride at 120-130° (Bertagnini, A. 100, 126):

$C_6H_5.CHO + CH_3.COCl = C_6H_5.CH:CH.CO.H + HCl$ .  
 Perkin showed that it might be more readily obtained by heating a mixture of benzaldehyde, acetic anhydride, and anhydrous sodium acetate:

$C_6H_5.CHO + (CH_3.CO)_2O = C_6H_5.CH:CH.CO.H + C_2H_5.O_2$   
 (C. N. 32, 258; C. J. 1877, 388). The cinnamic acid employed in the preparation of artificial indigo was at first manufactured by this method; but the process was afterwards improved by Caro (Ger. Pat. 17,467, and 18,232), who showed that cinnamic acid could be prepared by heating benzal chloride with dry sodium acetate, thus avoiding the use of the expensive acetic anhydride:

$C_6H_5.CHCl_2 + 2CH_3.CO_2Na$   
 $= C_6H_5.CH:CH.CO_2H + 2NaCl + C_2H_5.O_2$   
 1 part benzal chloride, and from 2 to 3 parts of finely powdered, fused sodium acetate (for which potassium acetate, or a mixture of the potassium and sodium salts may be substituted) are heated at 180-200° for from 10 to 20 hours in an autoclave furnished with a mechanical stirrer. The melt is mixed with water, rendered alkaline with caustic soda, and steam-distilled to remove volatile oils, after which the solution in the retort is filtered hot, and the cinnamic acid is precipitated with hydrochloric acid, filtered off after allowing the solution to cool, pressed, and finally purified by recrystallisation from boiling water or alcohol. A method patented by the Farbwerke vorm. Meister, Lucius and Brüning (Ger. Pat. 18,064) in which lead acetate is substituted for sodium acetate offers no advantages over the foregoing.

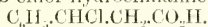
It may also be prepared from benzylideneacetone  $C_6H_5.CH:CH.CO.CH_3$ , which is readily obtained by the condensation of benzaldehyde with acetone under the influence of dilute caustic soda (Claisen, B. 14, 2471). When this compound is oxidised by warming it with sodium hypobromite, it is converted into cinnamic acid (Farbwerke vorm. Meister, Lucius and Brüning, Ger. Pat. 21,162).

By employing substituted benzaldehydes, benzal chlorides, or benzylideneacetones in the foregoing reactions, substituted cinnamic acids may be obtained.

Cinnamic acid may be extracted from storax by boiling in a retort 1.5 kilos. of storax with 2 lit. of caustic soda of 24 B. until no more oily drops distil over with the steam. In this process the styracine is hydrolysed, forming sodium cinnamate and cinnamyl alcohol, the latter being volatile with the steam. The aqueous liquid in the retort is separated and the residue repeatedly extracted with boiling water, after which the cinnamic acid is precipitated from the united aqueous solutions by hydrochloric acid and purified by recrystallisation (Beilstein and Kuhlberg, A. 163, 123). Precipitated cinnamic acid may be readily freed from adhering resin by recrystallising it from hot light petroleum.

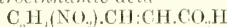
*Properties and Reactions*.—Forms slender needles or large transparent prisms melting at 133°. Boils at 300° (cor.). If rapidly distilled it scarcely suffers any decomposition, but by slow heating it is broken up into styrolene

$C_6H_5CH:CH_2$  and carbon dioxide. Sparingly soluble in cold, more readily in boiling water; easily soluble in alcohol. Forms crystalline salts closely resembling those of benzoic acid. Oxidising agents convert it first into benzaldehyde (distinction from benzoic acid) and afterwards into benzoic acid. When taken internally it is oxidised to benzoic acid and reappears in the urine as hippuric acid. By fusion with caustic potash it yields a mixture of benzoate and acetate. Unites with nascent hydrogen to form hydrocinnamic ( $\beta$ -phenylpropionic) acid, with bromine to form a dibromide, and with the hydrazids to form  $\beta$ -halogen-hydrocinnamic acids—thus  $\beta$ -chlor-hydrocinnamic acid



**Substituted cinnamic acids.** Of the substitution derivatives of cinnamic acid the only one of industrial importance is orthonitrocinnamic acid, which is prepared in the manufacture of orthonitrophenylpropionic acid (*v. INDIGO, ARTIFICIAL*). On a large scale cinnamic acid is first converted by heating with alcohol and concentrated sulphuric acid into ethyl cinnamate. The latter substance, which being a liquid is more easily manipulated in the nitration process than the solid cinnamic acid, is run in a thin stream into the calculated quantity of cold nitrosulphuric acid. The mixture of ortho- and para-nitrocinnamic ethers thus formed is dissolved in warm alcohol. On cooling, the para-compound crystallises out, whilst the ortho-compound remains in solution. The two ethyl salts are hydrolysed by heating with sulphuric acid. In this process the two isomerides are formed in approximately equal quantity.

*Orthonitrocinnamic acid*



is insoluble in water, sparingly soluble in cold, more readily soluble in boiling alcohol, from which it is deposited in crystals melting at  $240^\circ$ .

The *para*-compound melts at  $285$ – $286^\circ$  and is very sparingly soluble even in boiling alcohol. It cannot be used in the preparation of artificial indigo, and the attempt made to utilise it in the rosaniline manufacture has not proved industrially successful.

F. R. J.

**CINNAMON.** The inner bark of shoots of the *Cinnamomum zeylanicum*, nat. ord. *Lauraceae*, or true laurels. According to Percival it is imported principally from Ceylon; but in part also from Madras, Tellicherry, and, rarely, from Java. The bark-peelers select such branches as are three years old, and not more than two or three inches in diameter nor less than half an inch. The bark in drying rolls up into quills, many layers being inclosed in one quill. It is used as a condiment and yields a highly perfumed essential oil, *q. v.*, employed in the preparation of chocolate and for purposes of perfumery. Both the bark itself in its powdered state and the oil derived from it are frequently adulterated by cassia, *v. CASSIA*.

**CINNAMON BROWN or BISMARCK BROWN** *v. AZO-COLOURING MATTERS*.

**CINNAMON, OIL OF, *v. OILS, ESSENTIAL*.**

**CITRIC ACID**  $C_6H_8O_7$ . *Occurrence*.—This acid commonly occurs in the juice of many fruits, and in the sap of many plants.

*Synthesis*.—The acid has been prepared artificially by Grimaux and Adam (*C. J.* 38, 801).

A saturated solution of dichloroacetic acid was neutralised with sodium carbonate, and heated with two molecules of potassium cyanide. The resulting solution of dicyanoacetates was saturated with hydrochloric acid gas and heated in a water bath for 15 hours, the citric acid was then separated as calcium citrate by neutralisation with milk of lime.

*Properties*.—The crystallised acid of commerce has the formula  $C_6H_8O_7.H_2O$ . The crystals are large prisms belonging to the trimetric system. Their sp.gr. according to Buignet is 1.553. They deliquesce in damp air, and in perfectly dry air slowly lose the whole of their water. Different crystals (probably differently prepared) may lose water at very different rates (Warrington, *C. J.* 28, 928; Grosjean, 43, 331). According to Marchand (*J. pr.* 23, 60) crystals obtained from a saturated boiling solution have the formula  $2(C_6H_8O_7).H_2O$ . According to a later investigation by Saalandinaki (*B.* 5, 1100) the crystals from a solution long boiled are anhydrous. Citric acid is optically inactive. The ordinary crystallised acid dissolves in about half its weight of boiling water. Aqueous solutions of various strengths have, according to Gerlach (*F.* 1869, 295), the following sp.gr. at  $15^\circ$ :

Acid p.c.	Sp.gr.	Acid p.c.	Sp.gr.
1	1.0037	34	1.1422
2	1.0074	35	1.1467
3	1.0111	36	1.1515
4	1.0149	37	1.1561
5	1.0186	38	1.1612
6	1.0227	39	1.1661
7	1.0268	40	1.1709
8	1.0309	41	1.1756
9	1.0350	42	1.1814
10	1.0392	43	1.1851
11	1.0431	44	1.1899
12	1.0470	45	1.1947
13	1.0509	46	1.1998
14	1.0549	47	1.2050
15	1.0588	48	1.2103
16	1.0632	49	1.2153
17	1.0675	50	1.2204
18	1.0718	51	1.2257
19	1.0762	52	1.2307
20	1.0805	53	1.2359
21	1.0848	54	1.2410
22	1.0889	55	1.2462
23	1.0930	56	1.2514
24	1.0972	57	1.2572
25	1.1014	58	1.2627
26	1.1056	59	1.2683
27	1.1106	60	1.2738
28	1.1152	61	1.2794
29	1.1198	62	1.2849
30	1.1241	63	1.2904
31	1.1288	64	1.2960
32	1.1333	65	1.3015
33	1.1378	66	1.3071

A 25 p.c. solution boils at  $101^\circ.8$ , a 50 p.c. solution at  $105^\circ.8$  (Gerlach, *J.* 1859, 48).

At  $15^\circ$  the solubility of the crystallised acid in alcohol is as follows:

100	of 80 p.c. alcohol dissolve 87.
" 90	" " " 52.85
" 100	" " " 75.90

100 parts of anhydrous ether dissolve 9.1 of the crystallised acid.

*Decompositions.* When heated to  $175^{\circ}$ , acetone and carbonic oxide are evolved, the residue is aconitic acid,  $C_6H_4O_6$ ; the same acid is formed in small quantity when a solution of citric acid is long boiled (Dessaignes). When heat is continued beyond  $175^{\circ}$  an oily distillate appears, which yields crystals of itaconic acid  $C_6H_6O_6$ . By further heating, itaconic acid is transformed into an uncrystallisable oil, citraconic acid,  $C_6H_8O_6$ . Heated with sulphuric acid, carbonic oxide and acetone are given off, and an acid is formed not precipitated by baryta.

Solutions of citric acid are rapidly destroyed by fungi. According to F. Watts (C. I. J. 1886, 215) the action of *Saccharomyces mycoderma* on lime juice is to convert the citric acid into carbonic acid and water. According to I. Macaguo (G. 11, 443) an alcoholic fermentation in lemon juice does not affect the citric acid, but under the influence of bacteria the citric acid disappears, and acetic and propionic acids are formed.

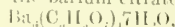
*Salts.*—Citric acid is tribasic, and forms in consequence three classes of salts. The salts with the alkali metals are readily soluble in water; the neutral salts of the alkaline earths are only sparingly soluble.

Calcium citrate  $Ca_3(C_6H_5O_7)_2 \cdot 2H_2O$  does not lose water at  $100^{\circ}$ . When precipitated in a crystalline state its solubility in water is 1 in 1180 at  $14^{\circ}$ , and 1 in 1730 at  $90^{\circ}$ – $100^{\circ}$ . When thrown down in an amorphous condition the solubility is greater, 1 in 707 at  $18^{\circ}$ , and 1 in 1123 at  $100^{\circ}$  (C. J. 28, 939).

When a solution of citric acid contains a ferrous, ferric, or aluminic salt, in not too great proportion, it may be made strongly alkaline with potash or soda without producing a precipitate. Such a solution may also be boiled with chalk without precipitating iron or aluminium, although a large part of the citric acid falls as calcium citrate. (With tartaric acid in the place of citric, iron is to a small extent precipitated by chalk in the cold, and entirely on boiling.) If, however, the ferric salt bears a large proportion to the citric acid, the whole is precipitated by chalk, even in the cold (C. J. 28, 990).

*Detection.*—Citric acid is best recognised when in a pure state by its yielding on heating an oily sublimate, which afterwards crystallises (itaconic acid). A solution of citric acid, neutralised with ammonia, gives no precipitate in the cold with calcium chloride, except after long standing; but on boiling, calcium citrate is precipitated. Calcium citrate, precipitated in the cold, is freely soluble in solution of ammonium chloride, and is precipitated therefrom on boiling. Alkali citrates do not reduce silver salts on boiling as tartrates do, or only to a trifling extent.

Kümmerer (Fr. 8, 298) recommends the detection of citric acid by the formation of a crystalline barium salt. To the free acid, or to the alkali salt, excess of barium acetate is added, and the whole heated on a water bath for several hours; the barium citrate,



will then be found in microscopic monoclinic prisms.

The tests for adulteration will be given at the close of this article.

*Estimation.*—When the quantity of citric acid in a solution is determined by alkalimetry, phenolphthalein should be used as the indicator; in coloured solutions red-brown turmeric paper (Thomson, C. I. J. 1887, 195) has been recommended. If neutral litmus paper is used, the alkali must be standardised with citric acid. The quantitative determination of citric acid by precipitation as calcium citrate will be described under the analysis of lemon juice.

#### RAW MATERIAL.

Citric acid is prepared from the fruit juice of three species of *Citrus*—the lemon, bergamot, and lime; the first of these is the principal source of citric acid. Concentrated lemon juice is chiefly imported from Sicily; a very little comes from Naples or Sorrento. Concentrated bergamot juice is prepared in Calabria, and exported from Messina. Concentrated lime juice is imported in small quantity from Montserrat and Dominica. The lemon juice from Sicily is prepared by pressing the inferior fruit, from which the rind has previously been removed, for the manufacture of essence. The so-called 'single' juice is then boiled down till its sp.gr. equals  $60^{\circ}$  on the citrometer (sp.gr. 1.24); it then forms a dark brown, rather syrupy liquid.

The total quantity of concentrated Sicilian and Italian juice imported to England in 1887 was equivalent to rather more than 3,400 pipes of 108 gallons; the amount used for the manufacture of citric acid was probably equivalent to 3,200 pipes. Of lime juice, about 2,000 puncheons of 110 gallons were imported in an unconcentrated condition, and used for the preparation of beverages. About 200 pipes of concentrated lime juice were imported, and employed for the manufacture of citric acid.

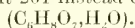
Lemon juice has its greatest acidity early in the season (November). The juice of the fine fruit, exported as lemons, has a sp.gr. 1.03–1.04; it contains free acid equal to 11–13 oz. of citric acid per gallon. The inferior fruit pressed in Sicily yields a juice containing at the beginning of the season about 9 oz. of free acid per gallon, and at the end of the season a good deal less.

There are other differences between the juice of fine lemons pressed in England, and the Sicilian juice employed for the manufacture of citric acid. The former contains very little combined organic acid, only about 2.5 p.e. of the total organic acid (free plus combined) present. In unconcentrated Sicilian juice the combined acid is about 7.9 p.e. of the total. Again, the English pressed juice contains hardly any organic acid save citric, only about 1 p.e. of the total organic acid being unprecipitable as calcium citrate. In Sicilian juice about 8 p.e. of the total organic acid is unprecipitable as calcium salt.

The concentrated lemon juice from Sicily is reckoned of standard quality when its sp.gr. is 1.24, and its acidity is equal to 64 oz. per gallon of nominal citric acid. In dealing with trade analyses it must, however, be borne in mind that the 'crystallised citric acid' of a trade certificate is not the crystallised acid of



commerce, but an acid containing only half the actual amount of water, an acid in fact having the atomic weight 201 instead of 210



No reason can be given for this practice, which should certainly be abolished. In the present article all quantities of citric acid will be expressed in terms of the common crystallised acid.

The concentrated lemon juice from Sicily contains pretty uniformly 7.8 oz. per gallon of combined organic acid, equal to about 10 p.e. of the total organic acid (reckoned as citric) present. Of the total organic acid about 10 p.e. is not precipitable as calcium salt, and is therefore not citric acid; this proportion is, however, by no means constant. Purchases of lemon juice are unfortunately still made on the basis of acidity, and not on the amount of precipitable acid present. Analyses of 895 pipes of concentrated lemon juice by Mr. Grosjean have been published (C. J. 43, 333). The average proportion of precipitable acid was 99.2 p.e. of the free acid, but the range of variation was considerable, individual parcels of juice giving 81.1, 85.8, and 103.6 of precipitable acid p.e. of free.

Concentrated Bergamot juice has a similar sp.gr. to lemon juice, but a lower acidity; it generally contains free acid equal to about 51 oz. of citric acid per gallon. The quantity of combined organic acid is apparently similar to that in lemon juice, namely 7.8 oz. per gallon; but the proportion of combined to total is higher, 12.13 p.e. The proportion of unprecipitable acid is about 13 p.e. of the total. Mr. Grosjean's analyses of 90 pipes of bergamot juice, show a mean of 98.4 of precipitable acid for 100 of acidity, the extremes being 95.4 and 101.4.

The unconcentrated Lime juice of Montserrat has a mean sp.gr. of 1.036; it contains according to Conroy (Ph. J. 1883, 606) an average of 7.81 p.e., or 12.54 oz. per gallon of free acid. The extremes observed were 6.70-10.05 p.e., equal to 10.7-16.1 oz. per gallon. The juice yields 0.43 p.e. of ash. It contains only a trace of sugar. Warington found the combined acid in two samples 5 p.e. of the total; 10 p.e. of the total acid was not precipitable.

Concentrated lime juice is a viscid liquid, sp.gr. 1.32, and with an acidity averaging about 94 oz. of citric acid per gallon. The combined acid is about 8.9 oz. per gallon. The unprecipitable acid is about 10.11 p.e. of the total. The precipitable acid bears a lower proportion to the free than is the case with either lemon or bergamot juice, the published analyses showing a mean of 93.8 of precipitable acid for 100 of free.

The nature of the organic acids, other than citric, present in lemon, bergamot, and lime juice has not been determined. A little formic acid and acetic acid have been detected in concentrated juice, but the principal acids other than citric are clearly non-volatile and have soluble calcium salts. The acids most probably present are malic and aconitic.

Besides lemon juice, some crude Calcium citrate, prepared in Sicily by precipitating lemon juice with chalk, is exported into England. It contains about 64 p.e. of citric acid.

## METHODS OF ANALYSING JUICE AND CITRATE.

1. *Acidity.* The commercial analysis of juice is confined to the determination of acidity. It is most important that the alkali (sodium hydrate) used should be actually standardised with citric acid, and the same indicator employed in standardising as in subsequent analyses. Powdered crystals of citric acid are taken, water carefully determined in one portion, while another is used for standardising the alkali. In determining water, the powdered acid should be heated for some hours at about 60° before exposing it to 100°; if this is not done the acid will melt, and lose the rest of its water with great difficulty. Warington recommended delicate litmus paper for determining the neutral point. F. Watts has since employed films of turmeric tincture on a white tile (C. I. J. 1886, 214). Thomson recommends red-brown turmeric paper.

2. *Combined organic acids.* The juice is neutralised with a known quantity of standard alkali, evaporated to dryness in a platinum basin, the residue gently ignited, the black ash treated with a known quantity (excess) of standard sulphuric acid, the whole boiled and filtered. The amount of unneutralised acid is then determined with alkali. We have now the neutralising power of the ash in terms of alkali; by subtracting the alkali added when neutralising the juice we obtain the amount of alkali corresponding to the bases of the organic salts which became carbonates on ignition. From the amount of these bases their equivalent in combined citric acid can be calculated.

3. *Precipitable citric acid.* This is for the manufacturer the only trustworthy method of analysis, but is in fact seldom adopted. Warington proceeds as follows:—15-20 c.c. of unconcentrated juice, or about 3 c.c. of concentrated juice, are exactly neutralised with sodium hydrate, the solution (about 50 c.c.) is brought to boiling in a salt bath, and a measured quantity of calcium chloride solution known to be rather more than sufficient for all the organic acids present added. After boiling for half an hour the precipitate is collected on a small filter, and washed with hot water. The filtrate and washings are then concentrated to 10 c.c. and the solution finally neutralised with a drop of ammonia. The second precipitate is collected on a very small filter, the filtrate being used for getting the precipitate on to the paper, which is finally washed about five times with a little hot water. The precipitates in their papers are then burnt at a low heat in a platinum basin, and the neutralising power of the ash determined with standard hydrochloric acid and alkali. The amount of citric acid which the base is equivalent to can then be calculated, three molecules of base being reckoned as equivalent to one molecule of citric acid.

4. *Analysis of calcium citrate.* The excess of chalk present is first determined by boiling about 4 grams with dilute standard hydrochloric acid in a covered beaker, and then adding standard alkali till feebly alkaline. Two grams of the citrate are then gently ignited in a covered platinum crucible, and the neutralising power of the ash determined by solution in standard hydrochloric acid, and titration with alkali. By de-

ducing from the neutralising power of the ash that due to the chalk previously determined, we find the amount of base which has to be calculated as citrate. This method presupposes that citrates are the only organic salts present. If it is preferred, the citrate may be dissolved in hydrochloric acid, the solution boiled, neutralised with soda, the calcium citrate precipitated by boiling in the salt-bath, and its quantity determined as in the case of juice.

The information here given respecting juice, calcium citrate, and the methods of their analysis, will be found in greater detail in C. J. 28, 925; 43, 331.

#### PROCESS OF MANUFACTURE.

The manufacture of citric acid from concentrated lemon juice is extremely simple. A proper quantity of whiting (levigated chalk) is mixed with water, and heated by steam in a wooden vat provided with a revolving agitator; the concentrated juice is then slowly pumped in, care being of course taken that the whiting is finally in small excess. The liquor never becomes neutral, however long boiling may be continued, or however great is the excess of whiting present; the adjustment of juice and whiting is therefore effected by ascertaining if the liquor effervesces with more whiting, or the precipitate effervesces with more juice. The amount of unneutralised acid is about 1-2½ p.e. of the original acidity of the juice. Pure citric acid is readily neutralised by whiting, malic and aconitic acid are not; the final acidity is thus possibly due to the presence of these acids. Citric acid, however, is not neutralised by chalk if phosphates, and especially ferrie phosphates, be present; this fact will also explain the result. It is not advisable to neutralise completely by the use of lime, as vegetable impurities are then thrown down which are afterwards difficult to separate.

The precipitated calcium citrate is washed with hot water on a filter. It is next brought by the addition of water to the state of thin cream, and decomposed, with constant agitation, by the addition of a small excess of sulphuric acid (sp.gr. 1.7). The occurrence of an excess of sulphuric acid is known by the liquor affording a precipitate with a strong solution of calcium chloride after some minutes' standing.

The citric acid liquor is then separated from the gypsum, which is washed on a filter. The liquor is evaporated in shallow leaden baths by steam heat. Much gypsum is at first deposited, from this the clear liquor is run off and further concentrated. When strong enough to crystallise, the hot liquor is run into a wooden tub provided with an agitator, and the liquor is kept in constant motion while cooling; by this process, known as 'granulation,' the citric acid is obtained as a crystalline powder. The mother liquor is again concentrated, and 'salt' again obtained by granulation. The process may be repeated a third time. The liquor is then too dark and impure for further crystallisation, and is known as 'old liquor.' The granulated citric acid when drained, and if necessary slightly washed, is redissolved, decolourised by heating with animal charcoal (previously freed from phosphates by hydrochloric acid), again concentrated to the crystallising point, and poured into

leaden trays about 3 inches deep; the crystals here formed are the citric acid of commerce. Citric acid thus prepared always contains a trace of lead.

The 'old liquor' is diluted with water, and the citric acid it contains precipitated with an excess of whiting, exactly as in the case of the original juice. The liquor is never neutralised by the whiting; this may be either due to aconitic acid formed during the heating of the citric acid liquors, or to the presence of ferrie or aluminic phosphate derived from the whiting.

Any considerable excess of sulphuric acid in the liquors, or any overheating, must be avoided, as occasioning decomposition of citric acid. The presence of iron or aluminium in the whiting also occasions loss, as citric acid holding iron or aluminium in solution is not precipitated by calcium carbonate. In consequence of the non-precipitation of iron or aluminium from citric solutions by whiting, the citric liquors of the factory remain nearly pure, however long the work may have been continued, a result very different from what happens in the case of tartaric acid; the purity of citric acid liquors is however obtained at the expense of some loss of citric acid. In a well-conducted factory the total loss during manufacture will amount to 12-15 p.e. of the citric acid in the juice.

The total quantity of citric acid made in the United Kingdom in 1887 was between 400 and 500 tons, of which about half was exported. About 15 tons were imported from Sicily; this was the only import. The acid is chiefly used by calico-printers; it is also employed in the preparation of effervescing drinks and in medicine. For some further particulars see J. Soc. Arts, 1876, 366.

**Adulteration.**—Citric acid is at times adulterated with tartaric acid. To detect adulteration Caillietet (C. J. 36, 674) adds 1 gram of the powdered acid to 10 e.c. of a cold saturated solution of potassium dichromate. If the solution remains unchanged in colour for ten minutes tartaric acid is absent. If tartaric is present the solution becomes brown. Pusck (C. I. J. 1885, 552) places 1 gram of the acid in a test-tube with 10 grams of pure oil of vitriol. The test-tube is placed in a water bath, and kept at 100° for one hour. If citric acid only is present the colour is lemon yellow. If tartaric acid is present the colour becomes brown. Both these tests are very delicate, and readily show 1 or ½ p.e. of adulteration. Tartaric acid may also be detected by adding a little solution of potassium acetate to a strong solution of the citric acid, and stirring.

The quantity of tartaric acid in an adulterated sample may be determined by adding 10 p.e. of potassium chloride to a strong solution of the acid, and precipitating the tartaric acid with citrate or acetate of potassium, with the precautions described under estimation of tartaric acid. R. W.

**CITRON, OIL OF.** v. OILS, ESSENTIAL.

**CITRONELLA OIL** v. OILS, ESSENTIAL.

**CITRONINE** v. NAPHTHALENE COLOURING MATTERS.

**CIVET.** An odoriferous substance resembling musk or ambergris obtained from the pouches situated between the anus and genital organs

of *Tiverra ciretta* of N. Africa, *V. Zibetha* of Asia, and *V. Basse* of Java. Is of the consistence of honey, and of a yellowish or brown colour. Contains stearin, olein, mucus, resin, volatile oil, and yellow colouring matter (J. Ph. 1824, 537).

**CLARET G, CLARET RED, v. AZO-COLOURING MATTERS.**

**CLAUSTHALITE** v. **SELENIUM, Occurrence;** also **LEAD.**

**CLAY.** (*Argille*, Fr.; *Thon*, Ger.) The term clay is applied to certain hydrated silicates of aluminium, resulting, for the most part, from the decomposition of the felspar in granite.

Economically, any argillaceous earth which possesses sufficient ductility and plasticity, when intimately mixed with water, to be fashioned like paste or worked in a potter's lathe, is called a clay.

Clays are generally sedimentary deposits, of every geological age from the Recent to the Silurian or even Cambrian, and are of every degree of hardness, from the soft drift which may be dug with a spade to those of the older formations which require to be blasted. The plasticity diminishes as the geological series is descended. Those clays, however, which are hard and rocky when first wrought, soon disintegrate on exposure to atmospheric influences and become plastic and ductile. Clay usually emits the peculiar odour known as 'argillaceous' when breathed upon or moistened; this is especially noticeable in the impure varieties.

Plasticity is an essential quality of clays. When powdered they are readily diffusible through water, forming a plastic ductile mass which may be moulded into any required shape, the more finely divided varieties possessing this property in a higher degree. At 100° C. clay loses its hygroscopic moisture, and contracts; the water is, however, reabsorbed on moistening. No chemically combined water is driven off even at 300° C. At a red heat, however, it becomes anhydrous and loses its plasticity, becoming rigid, porous, and incapable of taking up water except mechanically. Clays seldom occur in a state of purity, usually containing mica, quartz, undecomposed felspar, sesquioxide or protocarbonate of iron, lime, magnesia, organic matter, &c. The presence of much carbonate of lime constitutes a *marl*. The colour varies according to the constituents, from white, in the pure clays, to black, red, blue or purple, the usual colour being yellow or grey. The colour of the clay, however, is no criterion of the appearance of the burnt goods. The ultimate colour depends almost entirely upon the amount of iron present and the heat used in burning. Yellow clays contain hydrated sesquioxide of iron; they occur, usually, in surface deposits or where red or grey clays have been weathered. On ignition the anhydrous sesquioxide of iron is formed, with the production of a red colour. Red clays and marls contain the anhydrous iron sesquioxide; the red Keuper marls contain about 3 p.c., and the clay used for the Beauvais pottery contains about 20 p.c. of that oxide. Their colour is merely intensified by burning. Grey clays which contain iron pyrites lose sulphur, with formation of the sesquioxide, and become red on ignition; those containing

ferrous carbonate evolve carbon monoxide, producing the sesquioxide, and also become red. When containing less than 1½ p.c. of iron, they produce various shades of cream and buff; with 3 or 4 p.c. and upwards, they are used in the manufacture of terra cotta, encaustic tiles, &c. The presence of much organic matter, unless the baking is performed with free access of air, reduces the colour considerably on account of its reducing action on the ferric oxide. Carbonate and oxide of lime and magnesia have a corresponding effect; in fact, ground chalk is frequently added to clay which would burn red, for the production of yellow bricks. Ignition, so long as the iron remains in the form of oxide, serves to intensify the colour, but if sufficiently high to induce combination between the iron and silica, the colour is much reduced. The behaviour of clays under heat depends on the amount of lime, magnesia, and ferric oxide present. Clays which are very refractory become more fusible when mixed with small quantities of these oxides. The presence of excess of silica decreases the fusibility.

Clay is acted upon slowly by hydrochloric or nitric acids, but is soluble in strong sulphuric acid, with formation of aluminium sulphate, especially after gentle roasting. After strong ignition, however, it becomes insoluble. Even after ignition, it is dissolved by hydrofluoric acid with formation of aluminium fluoride, while the silicon passes off as silicon fluoride.

The presence of clay in soils exerts an important action on the growth of plants. Ammonia is retained by clay in such a manner that it cannot be removed except by an excessive amount of washing; in fact, clay will remove ammonia and many organic substances from manure, but still retains them in a form readily available for plants.

*Kaolinite*  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  is the essential constituent of all clays. It is found in Devon and Cornwall, in Anglesea and in the United States &c., massive and in veins.

When pure it is perfectly white, but it is frequently grey, yellow, brown, or greenish. Under the microscope it is seen to consist of thin translucent, flexible, inelastic, six-sided scales, isolated or aggregated in bundles. It has an earthy fracture and a pearly lustre, and is more or less unctuous and plastic according to the fineness of the particles. It is infusible in the porcelain furnace.

*Kaolin*, *China clay*, *porcelain clay*, *Cornish clay*, is the purest variety of clay. It was formerly obtained from a mountain in China, known as Kau-Ling (high ridge), whence its name.

It results from the decomposition of felspars containing but little iron, more especially from the soda felspars in granite.

Kaolin is worked in Cornwall and Devon, near St. Austell, on Dartmoor, at Bovey Tracey, at Balleswidden and other St. Just mines, at St. Yrieix near Limoges, &c., being produced principally by the weathering of *pegmatite*, a variety of granite containing but little mica and quartz.

It is a soft, friable, sectile, white mineral, showing the hexagonal crystals of *kaolinite* under the microscope, is somewhat meagre to



the touch, and forms a paste difficultly with water. When heated it hardens, but does not fuse in the porcelain furnace. The purest varieties are white, but it has frequently a brown, yellow, or grey colouring, or is dark from the presence of carbonaceous matter. The clay used by the Chinese is exceptionally pure.

Masses of soft granite are found in some instances decomposed to a depth of 100 feet, available for the workman, but the finer varieties are those which have been washed out and separated from the coarser impurities by water.

It always contains quartz, mica, undecomposed felspar, &c. For the separation of these impurities it is levigated with a stream of water, and the finer particles of kaolin which remain suspended after the impurities have been deposited are settled in 'pits' 30 or 40 feet in diameter and 7 to 10 feet deep. When these have become filled with the clay it is removed to stone tanks, often over 60 × 30 × 6 feet in size, and settled to a tenacious cream. It is thence removed to the 'dry,' where it is spread on porous tiles in a layer 9 inches thick at the fire end and 6 inches at the stack end, and dried before being worked up.

A white vitrifiable variety of partially decomposed granite is largely used by the porcelain makers under the names *porcelain stone*, *China stone*, and *Cornish stone*, and by the Chinese as *Petuntze*. The uses of kaolin are various. About one-third of the output is used in the manufacture of porcelain, it is largely used in paper-making and for filling the pores of calico, and in the manufacture of alum, aluminium sulphate, and ultramarine.

The fine mica and sand separated in the levigation of the kaolin are also used, the former for weighting coarse papers, paperboards, &c., and the latter with Portland cement as a concrete (v. J. H. Collins, J. Soc. Arts, 1876, 565).

The following analyses show the composition of *washed kaolin*:

Analyst	Ebelmen and Silvestre		Richardson
Locality	Chinese	St. Yrieix	Cornish
Silica . . .	50.5	48.37	46.32
Aluminium . .	33.7	34.95	39.71
Oxide of iron . .	1.8	1.26	0.27
Lime . . .	—	—	0.36
Magnesia . . .	0.8	trace	0.44
Potash and soda .	1.9	2.40	12.67
Water . . .	11.2	12.62	
	99.9	99.60	99.80

*Pipe-clay (potter's clay)* is a soft clay used without any addition in the manufacture of tobacco pipes. It is nearly free from iron, lime, and magnesia, and is therefore very refractory. It differs from kaolin in containing somewhat more silica. The following analyses by Weston show the composition of that worked at Poole in Dorsetshire. Silica 18.99, alumina 32.11, potash 3.31, lime 0.13, magnesia 0.22, ferrous oxide 2.34, moisture 2.33, combined water 9.63; total 99.36.

*Fire-clays* are extremely refractory clays. They usually underlie beds of coal, whence their

name, 'underclay.' They are dark in colour and contain roots of stigmaries &c. The beds vary in thickness from a few inches to several feet, are co-extensive with the coal seams, and are sometimes worked in conjunction with them, forming a valuable adjunct to a colliery, especially when worked on a large scale.

The following analyses show the composition of fire-clay. No. 1 is of Stourbridge clay, by C. Tooke; No. 2 is of Eisenberg clay, goods made of which were unaltered at the fusing point of platinum; and No. 3 is from the same locality, goods made of it swelling at that temperature (C. Bischof, D. P. J. 231, 35).

—	1	2	3
Silica (combined) .	65.10	5.11	30.53
„ (free) . .	—	84.59	34.19
Alumina . . .	22.20	5.40	24.02
Magnesia . . .	0.18	0.09	0.40
Lime . . .	0.14	0.20	0.37
Potash . . .	0.18	0.61	2.40
Iron oxide . . .	1.92	0.21	0.87
Phosphoric acid .	0.05	—	—
Water (combined) .	7.10	—	—
„ (hygroscop.) .	2.18	—	—
Organic matter . .	0.58	—	—
Loss on ignition .	—	3.74	7.38
	99.66	99.95	100.06

Fire-clay is usually greenish grey and dense, breaking into rocky masses and fragments. At the outcrop, where it has become weathered, it acquires a yellow colour and is found unsuitable for the best qualities of fire goods. Only those underclays which are very free from lime, magnesia, and iron are suitable for fire goods. The process of mining fire-clay resembles that of coal. Shafts are sunk to the seam and plant is erected as in coal mining, but on a smaller scale. Headings are driven out and a 'face of work' is opened if worked on the 'long wall' principle, or, as is the case in some districts, it is worked by 'pillar work.' The raising and working of fire-clay form an important industry in this country.

When brought to the surface, it is laid in heaps or spread in layers of a few feet in thickness, and allowed to weather and 'ferment' for a few months before use.

The clays of Stourbridge are the most refractory, but good fire-clays are obtained in Glasgow, Northumberland, Lancashire, Warwickshire, South Wales, and other localities.

Fire-clay is principally used in the manufacture of fire-bricks, gas retorts, crucibles, glass-house pots, saggars, &c., and, when ground, as a furnace-lining. Glazed sanitary pipes are made from an inferior fire-clay, and receive a salt-glaze at the end of the burning.

Certain siliceous fire-clays, which are comparatively free from iron, are used in the manufacture of a common enlinary ware, the treatment they receive being similar to that of the finer clays employed in pottery.

The raw material is brought from the mine or quarry, spread in thin layers and weathered for several months. It is then placed in tanks and worked with paddles, by hand or machinery,

and converted into a pulp or 'slip.' The finer portion is then pumped into flat tanks heated from below, and the water evaporated until the slip is of sufficient consistency to be cut into slabs and conveyed to the moulds or potter's lathe. The coarser particles remaining in the tank bottom are rejected.

*Plastic clay.* This term is applied to those beds of the Lower Tertiary or Eocene strata which occur between the London clay and the chalk. They may be recognised at Woolwich, Reading, Blackheath, Bognor, Isle of Wight, in the neighbourhood of Paris, &c. It is red, mottled, or purple, burning to a red. Some of our earliest pottery was manufactured from this clay, and it is still worked in Hampshire and in the Isle of Wight.

*Slate clay* occurs in Devon and Cornwall, differing considerably in different districts. It is massive, interspersed with mica, and of green or greyish colour. In one form it occurs hard, and readily cleavable into slabs or slates, and is used for roofing &c.; in another form, the 'killas' of the Cornish miner, it has an earthy fracture, is soft and frangible, and crumbles down when immersed in water for some time. When free from lime, magnesia, and iron, it is ground, reduced to a paste, and made into fire-bricks.

Chippings from the slate quarries are used in making a strong durable brick. They are reduced to a powder, forced into the required shape by a powerful press, and burnt in the ordinary manner.

*Common clays* are of very variable composition and colour, and are widely distributed. They occur in surface deposits as drift or boulder clay, or stratified, as in the older formations.

Brick-making is an exceedingly important industry. In Great Britain alone the annual production is estimated at thirty millions.

The common clays of the eastern, east midland, and some of the southern counties, usually produce light-coloured bricks, but the majority of clays burn to a red.

The clay used should be free from stones, but frequently contains a considerable amount of sand, sometimes 20 or 30 p.c. It is usually weathered, and well ground before use.

In some of the Midland counties vast deposits of red clays and marls are found, from which 'blue bricks' are made. These clays contain more iron, are denser, and require stronger machinery for working than red-brick clays. They are also subjected to a longer and more intense firing. The brick, after being moulded, receives a coating of mill dust before being dried, and salt is thrown upon the fires at the end of the baking to produce a better glaze, and to render the brick less absorbent. Blue bricks, from their great strength and imperishability, are largely used in engineering work. The following analysis by Henry shows the composition of a clay which produced good red bricks: Silica 55.40, alumina and iron oxide 24.00, carbonate of lime 2.70, carbonate of magnesia 1.30, water &c. 21.60.

*Chemical analysis of clay.*—About 2 grams of the finely powdered, air-dried soil is weighed in a large porcelain crucible or a watch-glass and

heated at 100°C. for some days. The loss found on weighing is calculated as moisture, or 'hygroscopic water.'

About 2 grams of this powder is then heated in a dish (platinum, if possible) with excess of concentrated sulphuric acid, for 8 or 10 hours, and evaporated to dryness.

The cold residue is boiled with water, the solution filtered, and the insoluble matter, consisting of sand, free hydrated silica, and the silica which was combined with the alumina, is washed, dried, and weighed. It is then boiled repeatedly with sodium carbonate solution in a dish and filtered, and the residue, which consists of sand only, is washed with hot water, then with water acidulated slightly with hydrochloric acid, and finally with pure water, dried, ignited, and weighed. This weight, subtracted from that of the total silica, gives the amount of combined silica and of free hydrated silica (which seldom exceeds 1 p.c.).

When titanium dioxide is present in the clay, a known weight of the residue from the treatment with sulphuric acid is heated with hydrofluoric and sulphuric acids, and the greater part of the silica volatilised as fluoride. The residue is fused with potassium bisulphate, dissolved in cold water, filtered if necessary, and boiled. The titanium dioxide is then reprecipitated; it is washed, dried, ignited, and weighed.

The filtrate from the treatment with sulphuric acid is treated with excess of lead nitrate solution, and, after standing for some hours is filtered from the precipitated lead sulphate. The excess of lead is removed from the filtrate and washings by a stream of sulphuretted hydrogen, and the solution evaporated to dryness and gradually heated to about 250°C. until nitric acid is no longer evolved. The residue consists of alumina, ferric oxide, and calcium, magnesium, and alkaline nitrates. It is moistened with concentrated ammonium nitrate solution, and heated on the water-bath until ammonia fumes cease to escape. The residue is treated with hot water, and the insoluble alumina and ferric oxide washed, dried, ignited and weighed. The alumina and iron may be separated in this residue as described under *Estimation*, art. ALUMINIUM.

The filtrate is treated with ammonium oxalate, and filtered after twelve hours or more, the precipitate is ignited and weighed as caustic lime. The filtrate is evaporated to dryness, ignited to expel ammonium salts, and treated with excess of oxalic acid. A small quantity of water is added and again evaporated to dryness, and ignited gently, to convert the magnesium oxalate into magnesia and the alkaline oxalates into carbonates. It is repeatedly treated with small quantities of water and the magnesia filtered off, dried, ignited, and weighed.

The filtrate is treated with a few drops of hydrochloric acid, evaporated, and gently ignited, and the small quantity of alkaline chlorides weighed. If it is desired to separate the potassium and sodium, the former may be precipitated by platinum chloride, or they may be indirectly determined by means of a weak standard solution of silver nitrate.

All the reagents used should be very pure and *absolutely* free from alkaline salts. The ammonium nitrate and oxalate, and the oxalic

acid should volatilise, leaving no white stain, on ignition on platinum foil.

The production of the finer clays in three districts during the last four years is as follows:

	Cornwall		Devonshire			Dorsetshire	
	Kaolin and China stone	Value	China clay	Potter's clay	Value	Potter's clay	Value
	Tons	£	Tons	Tons	£	Tons	£
1883	313,053	234,789	35,889	12,306	36,070	134,539	67,270
1884	298,796	221,097	58,487		39,479	120,000	60,000
1885	312,413	231,310	31,734	58,503	39,490	122,864	46,074
1886	290,270	217,710	32,180	31,927	43,177	122,557	45,958

*Exports of Clay from the United Kingdom.*

	1885		1886	
	Quantity	Value	Quantity	Value
	Tons	£	Tons	£
Russia . . . . .	11,125	11,082	8,875	9,018
Norway and Sweden . . . . .	8,446	7,611	6,320	5,946
Germany . . . . .	27,972	27,330	26,306	27,172
Holland . . . . .	32,480	31,345	31,267	29,685
Belgium . . . . .	34,958	33,668	31,026	30,224
France . . . . .	31,869	31,310	32,338	32,598
Spain . . . . .	4,794	5,531	4,188	4,479
Italy . . . . .	4,822	4,872	8,416	8,161
United States . . . . .	15,025	21,581	21,776	31,212
Other Countries . . . . .	12,014	16,670	13,815	18,646
Total . . . . .	183,505	191,051	184,357	197,141

**CLAY IRONSTONE** *v.* IRON, ORES OF.

**CLAY SLATE** *v.* SLATE.

**CLEVELAND IRONSTONE** *v.* IRON, ORES OF.

**CLICHY WHITE**, a white lead manufactured at Clichy, in France, *v.* *White lead*, art. LEAD.

**CLOVES, OIL OF**, *v.* OILS, ESSENTIAL.

**COAL** *v.* FUEL.

**COAL GAS** *v.* GAS, COAL.

**COBALT**. Symbol Co. At. w. 58·7 (Rothoff, Dumas, Russell, Winckler, Weselsky, Lee).

Cobalt usually occurs combined with arsenic or sulphur, and almost invariably associated with nickel and other metals. Free cobalt occurs only in meteorites.

The most plentiful and important ore of cobalt is *smaltine* or *tin white cobalt*, consisting of arsenide of cobalt, nickel, and iron. It occurs abundantly at Sehneberg and many other localities where bismuth is found (*v.* BISMUTH), in Bohemia, very pure at Tunaberg in Sweden, and free from nickel in Colorado. As triarsenide it forms *Skutterudite*  $\text{CoAs}_3$ . Sulpharsenide of cobalt occurs as *cobalt glance*, *grey cobalt*, or *cobaltine*, abundantly at Vena (Sweden) and in Norway; in smaller quantities in Silesia and Cornwall. As hydrated arsenate it forms *cobalt bloom* or *erythrite*  $\text{Co}_3\text{As}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ , found frequently as a peach-coloured incrustation on other arsenical ores, being produced by their decomposition. As sulphide, cobalt occurs in small quantities in *cobalt pyrites* and in *linnaitite*.

*Black earthy cobalt* is a hydrated oxide of cobalt and manganese. It is essentially a variety of *wad* (hydrated manganese oxide) containing sometimes as much as 40 p.c. of cobalt, and is imported into England from Missouri for the manufacture of smalt. Surface deposits con-

taining oxides of cobalt and of nickel occur at New Caledonia with veins of chrome ore and nickel and magnesium silicates; it is smelted on the spot and imported as a regulus to England. Cobalt occurs in small quantities in many other minerals; as oxide in black oxide of manganese; as arsenide in mispickel, sometimes to the extent of 10 p.c.; in selenide of lead, and in cerite and Flemish coal.

*Extraction*.—Metallic cobalt is not at present used to any extent in the arts, though its utility is becoming more fully recognised. It may be prepared by the ignition of the oxide with charcoal; it then contains carbon. Pure cobalt is prepared by igniting the oxalate of cobalt  $\text{Co}(\text{C}_2\text{O}_4)_2$ , when the carbon and oxygen pass off as carbonic anhydride, leaving the pure metal as a powder. A button of the fused metal may be obtained by fusion of the oxalate alone, or of the oxide mixed with charcoal under a layer of powdered glass containing no lead or other reducible metal; the fusion is preferably performed in a lime crucible at the highest temperature of a furnace. Cobalt is also produced as a grey metallic powder by igniting the oxide at a red heat in a current of hydrogen. If too low a temperature has been used, the metal produced is *pyrophoric*, igniting and becoming reoxidised in contact with the air.

*Properties*.—Cobalt is a white, slightly reddish metal, similar in properties to iron. It is the most magnetic metal after iron, its magnetism, according to Pouillet, not being destroyed at a red heat.

Pure cobalt is harder and more tenacious than iron; from a button of the metal prepared from the oxalate, Deville has obtained cobalt



wire of nearly double the tenacity of iron. Valenciennes states that cobalt, after fusion and annealing, may be rolled into spiral bands like good iron (C. R. 70, 607). Cobalt melts at  $1,500^{\circ}\text{C}$ . (Pictet)—i.e., about the temperature at which English hammered iron fuses. Its sp.gr. varies between 8.5 and 8.9. It is slowly soluble in hydrochloric and sulphuric acids, with evolution of hydrogen, quickly soluble in nitric acid. The powdered metal combines, when heated, with chlorine, bromine, and iodine. It decomposes steam at a red heat.

Cobalt may be deposited as a fine lustrous coating on metals by the electrolysis of a neutral solution of the double sulphate of cobalt and ammonia, using a weak current and an anode of cobalt (A. GaiFFE, C. R. 1878). The presence of ammoniac chloride appears to hinder, while ammoniac sulphate assists, the deposition. The deposit of cobalt is harder, more tenacious, and of greater beauty than that of nickel (Troost). Cobalt plating is stated to be practised as 'superior nickel plating.'

For the properties of cobalt containing other metals, *v. Alloys of cobalt*.

*Detection.* All ores and compounds of cobalt impart a blue colour to a bead of borax on ignition; if present in too great excess the bead appears black. Heated on charcoal with reducing flux, all substances containing cobalt produce metallic particles which are attracted by a magnet (distinction from all other bodies except iron and nickel).

Salts of cobalt, when *strongly* ignited with alumina before the blowpipe, give a fine blue colour (Thenard's blue). Sulphuretted hydrogen produces no precipitate in an acid solution, but gives a black precipitate of sulphide in alkaline solutions. In a solution containing free acetic acid, potassic nitrite produces a yellow precipitate (*v. Cobalt yellow*), the whole of the cobalt being thus precipitated on standing in a warm place for some time.

*Estimation.* Ores containing cobalt are usually very complex; they almost invariably contain nickel and many other metals from which the separation is difficult. The following scheme will serve for the estimation of both cobalt and nickel in any mineral, though in the case of certain ores it may be somewhat simplified.

From 2 to 7 grams of the finely-ground ore are weighed, and, if much sulphur and arsenic are present, roasted in a porcelain crucible in a muffle. The residue is boiled with hydrochloric acid containing a little nitric acid until the metallic oxides are dissolved; the solution is diluted, nearly neutralised with ammonia, and boiled with sodium acetate solution, whereby the iron and aluminium are precipitated as acetates containing the greater part of the arsenic (as arsenate of iron) and a little nickel and cobalt. The solution is filtered, and the precipitate redissolved in hydrochloric acid and reprecipitated as before, the precipitate being this time free from nickel and cobalt. The two filtrates are mixed, just neutralised with ammonia, and sulphuretted hydrogen gas passed; thus the cobalt, nickel, zinc, copper, bismuth, &c. are precipitated as sulphides, leaving the manganese and the alkaline and earthy metals in solution. The precipitate is filtered, washed, dried, and roasted, the oxides

so produced dissolved in hydrochloric acid, and treated with sulphuretted hydrogen; the copper, bismuth, lead &c. are thus precipitated and filtered off.

The solution is boiled till free from sulphuretted hydrogen, and the two metals coprecipitated by the addition of potash to the boiling solution; the precipitate is filtered and washed, nearly dried, and separated as far as possible from the filter. The precipitate is digested in a dish with dilute hydrocyanic acid, then with potash solution, and again with hydrocyanic acid, and warmed until no further solution occurs. A minute quantity of residue is left, consisting of paracyanogen and a small quantity of the oxides of nickel and cobalt; it is added to that still remaining on the filter paper, and the whole washed, dried, ignited, and weighed.

The solution containing the two metals is boiled to expel the excess of acid, and consists of cobalticyanide of potash and double cyanide of nickel and potash. Precipitated yellow mercuric oxide is added, and the solution boiled for some time. The nickel is thus precipitated, partly as cyanide and partly as sesquioxide. It is filtered, washed, dried, ignited, and weighed as protoxide of nickel  $\text{NiO}$ . The filtrate is nearly neutralised with nitric acid, and a neutral solution of mercurous nitrate added in excess. The cobalt is thus precipitated as cobalticyanide of mercury, which is washed, dried, and ignited in an open crucible until of constant weight. The product consists of  $\text{Co}_3\text{O}_4$ .

From the proportions of cobalt and nickel thus found, the amount of each in the residue on the filter paper &c. which has been weighed may be calculated, and added to the amounts directly determined.

(See further, Hadow, C. N. 2, 85, and Crookes, *Select Methods in Chemical Analysis*, 2nd edit. 253-275.)

**Alloys of cobalt.** Cobalt unites with incandescence on fusion with *antimony* or *arsenic*, forming brittle, iron-grey alloys. The principal ore of cobalt, smaltine, consists of an arsenide of cobalt  $\text{CoAs}_2$ ; it is tin-white, hard, very brittle, and melts at a red heat. A triarsenide occurs as *skutterudite*  $\text{CoAs}_3$ .

With *copper*, cobalt is stated by Valenciennes to produce very ductile alloys which, when annealed may be hammered out and which melt at the same temperature as copper. A somewhat ductile violet alloy is produced by fusion of *tin* with cobalt.

With *gold* even a small quantity of cobalt produces a brittle alloy, that containing 1 part gold and 17 parts cobalt is dark-yellow and very brittle (Hatchett).

With *iron* a very brittle alloy is formed. A fusible alloy is produced with platinum, and a silver-white magnetic amalgam with mercury, which is used in dentistry. Cobalt does not alloy with silver, lead, and bismuth, the metals separating into two layers, each retaining a small quantity of the other metal.

According to Fleitmann (B. 12, 454, and Bl. 32, 667) the addition of  $\frac{1}{2}$  p.e. of magnesium to molten nickel or cobalt renders it malleable, ductile, and highly susceptible of polish; it can be welded with steel or iron and rolled into thin sheets without separation.

It is also possible to alloy cobalt and nickel with manganese with the production of valuable properties. For this purpose commercial manganese or ferro-manganese may be used, the presence of iron not being injurious. From 2 to 5 p.e. of the manganese is added in small portions to the molten metal; much gas is evolved after each addition, and the metal is poured into moulds when tranquil (v. Huntingdon, S. C. I. 1882, 258).

It is stated that when in the molten condition cobalt and nickel take up both carbon and oxygen, but evolve the greater part of the latter substance on cooling, leaving a porous metal containing carbon. A method has been patented whereby this carbon is said to be eliminated. The porous cubes of metal are immersed in a 4 p.e. solution of alkaline manganate or permanganate, dried and melted in a crucible at a high temperature. The carbon is said to be thus oxidised and removed, and the metal takes up a small quantity of oxygen. As soon as the metal flows easily a little black flux and charcoal, or a small quantity of aluminium, or the calcium zinc produced in Caron's process is added, and the oxygen thus removed (D. P. J. 1881, 251-315).

**Oxide of cobalt  $\text{Co}_3\text{O}_4$ .** This is the only oxide of cobalt of importance in the arts. It is prepared in large quantities from the ores of cobalt, and from *speiss* in the separation of nickel.

Several methods are recommended for the extraction from the ores.

1. *Laugier's method.* The powdered ore is roasted and dissolved in nitric acid or in dilute hydrochloric or sulphuric acid, containing if necessary a little nitric acid, filtered and evaporated nearly to dryness. A large proportion of the arsenic is thus separated as arsenious oxide; the liquid is diluted, decanted from the residue, and treated with sulphuretted hydrogen for the precipitation of copper, arsenic, bismuth, and tin. The solution is filtered, heated until the sulphuretted hydrogen is evolved, and the iron oxidised. Sodium carbonate is then added and the nickel and cobalt precipitated as carbonates together with oxide of iron, the precipitate well washed, digested with excess of solution of oxalic acid and filtered; the soluble ferric oxalate is thus separated from the insoluble oxalates of nickel and cobalt. The latter are triturated with ammonia and dissolved in excess of that substance by agitation and warming. The solution is filtered and exposed to the air for several days; the whole of the nickel is thus precipitated with a little cobalt. This small amount of cobalt may be removed by re-solution in ammonia and re-exposure to air. The solution containing the cobalt is evaporated to dryness and ignited in the open air with the production of very pure cobalt oxide.

2. An improvement introduced by Berthier much reduces the amount of sulphuretted hydrogen required for the precipitation. The solution obtained as above is mixed with a dilute solution of a ferric salt, and then with small successive portions of a solution of potassium carbonate. The precipitate at first produced consists of the light-coloured arsenate of iron, but at last it changes to the brown hydrate of

iron. In this manner, with the proper quantities of chloride of iron and of carbonate, nearly the whole of the iron and arsenic may be precipitated. Excess of potassium carbonate must be avoided, or the nickel and cobalt will come down. The bismuth, copper, &c., are then precipitated by a current of sulphuretted hydrogen, a much quicker operation in the absence of arsenic, and the operations continued as in 1.

3. According to Liebig's process (P. 18, 164) the finely powdered cobalt ore is carefully roasted, and one part of ore added in successive small portions to three parts of potassium bisulphate heated to the melting-point. The pasty mass so produced is then heated more strongly until fumes cease to be evolved and the mass fuses quietly. In this way the arsenic is converted into insoluble arsenate of iron: if too small a quantity of iron is present to combine with the whole of the arsenic a little ferrous sulphate is added before the fusion, otherwise a portion of the cobalt will remain combined with the arsenic. During the ignition the greater part of the nickel is converted into oxide; this conversion is not, however, complete in the presence of potassium sulphate, so the resulting cobalt oxide always contains nickel. The mass is ladled from the crucible with an iron spoon, cooled, and broken, boiled with water, filtered from the insoluble arsenate of iron, &c., and the heavy metals precipitated by sulphuretted hydrogen. That gas is then boiled off and the cobalt precipitated with potassium carbonate and ignited to oxide.

4. Wöhler (P. 6, 277) recommends the fusion of the powdered ore with 3 parts potassium carbonate and 3 parts sulphur. The metals are thus converted into sulphides. Care must be taken not to heat the mass sufficiently to fuse the cobalt sulphide, or it is difficult to separate it from the soluble impurities. The potash becoming converted into sulphide combines with nearly all the arsenic, forming soluble sulpharsenate of potash. The powdered mass is frequently exhausted with water and the residue again fused and washed, to remove the last traces of arsenic. It is then dissolved in nitric acid or in a mixture of sulphuric and nitric acids, and treated as in the former methods.

5. For the separation of cobalt from earthy ores, in which it occurs as oxide together with manganese, Waackneröder (N. Br. Arch. 16, 133) uses the following process. The mineral is dissolved in hydrochloric acid and the heavy metals precipitated with sulphuretted hydrogen and filtered, the solution boiled with nitric acid to oxidise the iron, which is then precipitated by the addition of sodium acetate and the cobalt precipitated from the filtrate by sulphuretted hydrogen. Or the cobalt together with the manganese and zinc may be precipitated with alkaline sulphide and the precipitate digested with dilute hydrochloric acid; the sulphides of the latter metals are thus dissolved while the greater part of the cobalt remains as sulphide from which the oxide may be obtained by roasting. Nickel, if present in the ore, will remain with the cobalt in this process.

The method generally adopted by manufacturers for the separation of cobalt in the extraction of nickel appears to be a variation of Berthier's process. The *speiss* from the prepara-

tion of smalt or the roasted ore is fused with fluor-spar and chalk to produce a richer matt containing less iron. It is then ground and thoroughly roasted to produce oxides and expel arsenic and sulphur, dissolved in hydrochloric acid and diluted with water. A small quantity of bleaching powder is added to oxidise the iron, which is then precipitated with the remaining arsenic by milk of lime. The liquid is decanted from the precipitate, the heavy metals precipitated with sulphuretted hydrogen, the solution decanted from the precipitate, and the cobalt precipitated as oxide from the solution by the addition of bleaching powder. The precipitate usually contains small quantities of iron and nickel, but the greater part of the latter is left in solution and subsequently precipitated by the addition of potash (Louyet).

Oxide of cobalt is used for the preparation of the salts of cobalt and of smalt, and by enamellers and porcelain manufacturers for the production of the finest blue glaze and colour on porcelain, glass, and other vitrifiable substances. The presence of  $\frac{1}{1000}$  of this substance imparts a bluish tinge to clear glass.

The presence of other oxides has an injurious effect on the colour produced by this substance (*v. Smalt*), it is therefore necessary, for the more delicate work, to ensure its complete freedom from such impurities.

When heated strongly with magnesia it produces a pink mass; with alumina a fine blue (Thenard's blue); and with zinc oxide a green (Rimmann's green). *Zaffre* consists of a very impure oxide of cobalt produced by roasting the ore. It is usually mixed with 2 or 3 parts of fine sand or ground quartz, and is used for the same purpose as smalt for the coarser work.

**Cobalt blue, Cobalt ultramarine.** Thenard's blue. The composition of this pigment varies considerably according to the method of manufacture. It consists sometimes of the oxides of cobalt and aluminium; at other times it contains phosphate or arsenate of cobalt.

It is prepared by first precipitating a solution of a cobalt salt, usually the nitrate, free from iron and nickel, with potassium or sodium phosphate or with sodium arsenate. The gelatinous violet precipitate is thoroughly washed and well mixed with 3 to 5 volumes of freshly precipitated, well-washed alumina (when arsenate of cobalt is employed, a larger proportion of alumina may be added). The mixture is dried until it becomes brittle, and calcined at a cherry-red heat for thirty minutes in a well-covered clay crucible. In order to prevent the possibility of entrance of reducing gases, which much injure the value of the product, Regnault has recommended the addition of a little mercuric oxide before the ignition. This becomes decomposed and evolves oxygen, which effectually prevents reduction, while the mercury escapes as vapour (Regnault, *Cours Élém. de Chimie*, 3, 150).

The alumina used is precipitated from a solution of alum free from iron by the addition of sodium carbonate.

A similar but less fine colour is produced by the simultaneous precipitation of the oxides of cobalt and aluminium by the addition of sodium carbonate to a mixture of cobalt nitrate

and alum; the mixed precipitate is washed and treated as above.

According to the process recommended by Binder (*Technologie*, 5, 55), the oxide of cobalt is precipitated by the addition of the requisite quantity of ammonia to a solution of pure cobalt chloride. The washed precipitate is mixed with alumina as before, dried, and calcined at a red heat in a clay crucible for two hours.

Thenard's blue is non-poisonous, of a fine ultramarine colour; the presence of excess of cobalt imparts a somewhat greenish tinge. It has, however, the disadvantage of appearing violet in artificial light. It is one of the most permanent blue pigments, being unaltered by acids or alkalis, and is largely used as an oil and water colour.

**Ceruleum, Céline, Bleu céleste**, is a corresponding colour containing oxide of tin and usually calcium sulphate. Its general composition is said to be oxide of tin 49.66, oxide of cobalt 18.66, sulphate of lime and silica 31.68.

It is a fine light-blue pigment of slightly greenish tinge, of greater density than Thenard's blue, and retains its colour in artificial light.

**Cobalt green, Rimmann's green.** The constitution of this pigment corresponds to that of Thenard's blue, with the substitution of zinc oxide for alumina.

It is prepared by precipitating a solution of pure cobalt chloride containing 100 grams of the protoxide of cobalt per litre (*i.e.* a 10 p.c. solution), with phosphate, arsenate, or, less satisfactorily, carbonate of sodium, mixing the well-washed precipitate with zinc oxide, drying and calcining. It may also be prepared by precipitating a mixture of zinc sulphate and cobalt nitrate with alkaline carbonate, washing and igniting the precipitate, or by evaporating a solution of a cobalt salt with zinc oxide and igniting the residue.

R. Wagner (*Technologie*, 18, 409) gives the composition of a fine green prepared by him as zinc oxide 71.68, phosphoric oxide 8.29, cobalt protoxide 18.93.

Rimmann's green is a fine permanent pigment; its colour varies through many shades according to the proportion of zinc present, the darker greens containing less of that substance. It is non-poisonous and unacted upon by acids or alkalis, but is attacked by ammonia. Rimmann's green, on account of its high price and the number of other permanent greens, is no longer used as a pigment. Another permanent green pigment used in porcelain-painting is said to be prepared by the calcination of a dried mixture of the following proportions of the freshly precipitated substances: 20 cobalt carbonate, 40 alumina, 20 chromium oxide.

**Cobalt bronze** is a phosphate of cobalt and ammonia, of a violet colour, with a bronze like metallic lustre.

**Silicates of cobalt.** A silicate of cobalt is produced by the addition of silicate of soda (soluble glass) to a cobalt salt. It produces a blue pigment well suited for painting on glass and porcelain.

**Smalt.** *Bleu d'azur, Bleu de Saxe.* This important substance consists of silicate of cobalt and potash.



In the preparation of smalt at Saxony smaltine is principally used. In Norway and Sweden the principal ore is cobaltine. The general process is identical for both ores.

The selected ore is powdered, freed from the lighter earthy impurities by washing, and placed, in charges of about 3 cwt., in a layer of 5 or 6 inches thick on the bed of a reverberatory furnace or in a muffle. It is then roasted, and the sulphur and arsenic expelled as oxides, the latter being condensed in chambers through which the fumes are passed. The roasting must be discontinued when sufficient arsenic is left to combine with the less oxidisable metals, especially copper and nickel, while the greater part of the cobalt is converted into oxide. In order to ascertain whether the roasting has proceeded sufficiently, a small portion is occasionally tested and the process stopped when the finest tinted glass is produced. The material is then ready for fusion for 'smalt.'

The fluxes used consist of powdered quartz and potassium carbonate. They must be of great purity, as the presence of lime and many other substances impairs the beauty of the colour. The quartz is first heated to redness, plunged into water, and thus disintegrated, and powdered in a mill. It is then suspended in water and allowed to subside for a short time, and the liquid, which contains most of the iron and other impurities still suspended, is poured off; this operation is repeated until a pure quartz powder is obtained.

The proportions of the ingredients used vary extremely according to the richness of the ore and the colour required. The potassium carbonate used generally amounts to about  $\frac{1}{3}$  of the weight of ore and quartz together. White arsenic is usually added to oxidise any protosalt of iron and thus prevent the injurious effect of that substance on the smalt, and to otherwise heighten the colour of the product. The exact amount of each of these substances is found by a test fusion and comparison with a smalt of the required colour.

The smalt furnace is similar to a glass oven; it usually contains eight crucibles. The pots are of very refractory clay, free from lime, and capable of holding  $\frac{1}{2}$  cwt. When charged, they are strongly heated and the mass fuses in about 8 hours; it is frequently stirred to render it homogeneous and to break the crust which forms on the surface. At a white heat combination occurs, the quartz and potash react with the production of fusible silicate of potash, which dissolves the oxide of cobalt forming the blue 'smalt,' while the mixed arsenides of nickel, copper, and iron, with the small quantity of arsenide of cobalt which is always present, fuse and form a brittle metallic looking *speiss* beneath the smalt. This usually contains about 3 p.c. of cobalt and a considerable quantity of nickel, and is used for the preparation of the latter substance and of cobalt oxide. The mass is left at a white heat for some time without stirring, to allow the *speiss* to settle, and ladled out with long-handled iron ladles into vessels of cold water. It is thus rendered granular, brittle, and easy to pulverise. When nearing the bottom of the crucible the ladle contains both *speiss* and smalt; the former,

being much more fusible, is poured first from the ladle, from beneath the smalt into a niche in the side of the furnace, whence the dense fumes of arsenic &c. which it evolves pass up the chimney.

The blue glass is next powdered with granite stampers, or ground between granite millstones under water, and the product passed through a series of depositing vats. In the first vat it remains for a short time only, thence it passes to a second for a somewhat longer time, to a third for about 15 minutes, to a fourth and fifth for a corresponding period, and finally to a sixth vat where it is allowed to deposit completely. The deposit in the first vat is returned to the mill and reground, that in the second and third is the best marketable smalt, while in the fourth and fifth vats a lighter-coloured deposit, sold under the name *eschel*, is produced. The deposit in the last vat is not marketable and is usually resmelted.

The marketable deposits are again washed, deposited, dried, powdered and sifted. About three-fifths of the glass taken from the pots is thus available. The presence of other oxides than those of cobalt and potash, even in small quantities, exerts a powerful influence on the colour of the smalt. Baryta produces an indigo tinge; sodium, calcium, and magnesium produce a reddish shade; iron, a blackish green, very prejudicial to the brighter-coloured smalts; manganese violet, nickel violet but less intense; copper, zinc, bismuth, and antimony, dull shades.

The composition of smalt varies considerably; the silica is usually from 56-70 p.c., potash 12-22 p.c. and cobalt 6-16 p.c. The following analyses by Ludwig (J. pr. 51, 129) are of interest:—

—	Norwegian deep coloured smalt	German deep coloured	German pale coarse
Silica . . .	70.83	66.20	72.12
Potash and soda .	21.41	16.31	20.04
Cobaltous oxide .	6.49	6.75	1.95
Alumina . . .	0.13	8.64	1.80
Protoxide of iron .	0.21	1.36	1.40
Arsenious acid .	trace	—	0.08
Water and carbonic acid .	0.57	0.92	0.16
	100.00	101.18	97.85

Smalt is a very permanent blue pigment, largely employed for the production of blue colours with vitreous substances and in painting, both for delicate and coarse work. It was formerly much used for colouring starch, paper, &c., but for this and many other purposes it is now almost superseded by the far less permanent artificial ultramarine.

**Cobalt yellow** consists of a double nitrite of cobalt and potassium, prepared by the addition of potassium nitrite to a solution of a cobalt salt acidulated with acetic acid. Its composition varies with the proportions used and the strength of the solution, Erdmann and Sadtler state

that when precipitated from a solution containing much acetic acid it consists of  $\text{Co}_2\text{K}_6(\text{NO}_2)_{12}$  with a variable amount of water.

Cobalt yellow is a bright yellow crystalline powder, very free from impurities, unacted upon by cold water or cold acids, and but slowly blackened by sulphuretted hydrogen.

It forms a fine pigment for artistic purposes. When used for painting porcelain it produces the usual blue colour on baking, which, on account of the purity of the substance, is of great beauty.

**Salts of cobalt.** The soluble salts of cobalt are prepared by solution of the oxide, carbonate, or metal in the various acids. They are generally pink and deliquescent, forming pink solutions when dilute, but when dried or in concentrated solution they are blue. For this reason, solutions of nitrate and other salts of cobalt are used as sympathetic inks, such writing being almost invisible until brought near a fire, when the letters appear blue. They gradually reabsorb moisture and again become invisible.

When ammonia is added to a solution of a cobalt salt oxygen is absorbed, giving rise under various conditions to many complex series of salts containing ammonia and different oxides of cobalt.

**Cobaltous chloride**  $\text{CoCl}_2$  is prepared by dissolving the oxide or carbonate in hydrochloric acid and evaporating the solution. According to the temperature at which it crystallises it may contain 6, 4, or 2 molecules of water of crystallisation, the latter at the higher temperatures.

Cobaltous chloride is soluble in water or alcohol. A strong solution, or a weaker solution containing strong hydrochloric acid, is of a blue colour.

**Cobaltous sulphate**  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  is prepared by solution of the oxide or carbonate in dilute sulphuric acid. It crystallises in red crystals isomorphous with magnesium sulphate, soluble in 21 parts of cold water.

**Cobaltous nitrate**  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is a red deliquescent crystalline salt prepared by dissolving the oxide in nitric acid. It is very soluble in water, the solution being used as a reagent in blowpipe analysis.

**COBALT BLOOM.** *Erythrite*; *Hydrated cobalt arsenate*; v. COBALT.

**COBALT BLUE** or **THENARD'S BLUE** v. COBALT.

**COBALT BRONZE** v. COBALT.

**COBALT GLANCE.** *Grey cobalt*; *cobaltine*. *Sulpharsenide of cobalt*; v. COBALT.

**COBALT GREEN** or **RINMANN'S GREEN** v. COBALT.

**COBALT PYRITES** v. COBALT.

**COBALT SPEISS** v. COBALT.

**COBALT ULTRAMARINE** or **COBALT BLUE** v. COBALT.

**COBALT YELLOW** v. COBALT.

**COBALTINE** v. COBALT.

**COCAINE** v. VEGETO-ALKALOIDS.

**COCCIN** v. AZO-COLOURING MATTERS.

**COCCININ** v. AZO-COLOURING MATTERS.

**COCCULUS INDICUS** or **INDIAN BERRY** is the fruit of the *Menispermum cocculeus* (Linn.), *Anamirta cocculeus* (Wight and Arnott), nat. ord. *Menispermaceae*, a tree growing upon the coasts of Malabar, Ceylon, &c. The berry is about the size of a large pea and of a dark-grey colour.

It possesses strong poisonous and narcotic qualities from the fact of its containing about one-fiftieth part of its weight of picrotoxin, and has been employed to increase the bitterness as also the inebriating effect of beer. It is, however, exceedingly deleterious to health, and the use of it for this purpose has been prohibited by the legislature under heavy penalties.

Besides picrotoxin, Schmidt and Löwenhardt (B. 14, 817) obtained from the seeds of *cocculus indicus* *cocculin*  $\text{C}_{17}\text{H}_{23}\text{O}_{10}$  crystallising in white needles, sparingly soluble in hot water, insoluble in cold water, alcohol, and ether. It is probably identical with Barth and Kretschy's *anamirtin*  $\text{C}_{16}\text{H}_{21}\text{O}_{10}$  which they regarded as a constituent of picrotoxin.

*Cocculus indicus* berries contain *menispermine*, *paramenispermine*, and *picrotoxin v. Picrotoxin*.

**COCHINEAL**, the insect which produces the red dyestuff known as carmine (*q. v.*). As found in trade it is the body of the female cochineal insect which lives on a species of cactus growing in Spain, Algeria, West Indies, &c. During life the insect is about the size of a small ladybird. It is rather long, compressed, equally broad all over, wingless, and marked behind with deep incisions and wrinkles. The cochineal insect has six feet, which nevertheless are only of use directly after birth. It fastens itself upon the plant by means of a trunk placed between its forefeet, and remains there till it dies. The sap of the plant provides this little animal with nourishment. The male cochineal insects resemble the female only during the larva state. They change into the chrysalis, and soon come forth as small red flies. The female then lays some thousands of eggs, and becomes covered with a white powder. She protects the eggs under her body, and hatches them, so to speak, in this way. When the young insect appears the mother dies. The young are now in the larva state, and the sex cannot be discerned. They lose their skin several times, and the female then fixes herself on the plant. The males, after passing through the pupa state, are winged. Their whole period of life is from two to three months. The cochineal insects are gathered shortly before they lay eggs, and they are then very rich in colouring matter. Only sufficient eggs are laid as may serve to reproduce the insect. They are killed with hot water or steam, and dried in the sun, in ovens, or on plates. The dead females are also collected. They have a brown, red, white, or black colour, and lose in the drying two-thirds of their weight. After drying the cochineal is sieved. About 70,000 insects go to make a pound of cochineal (S. C. I. 1, 181).

There are many different kinds of cochineal in the market, and it is frequently adulterated, chiefly with barium sulphate and with half-exhausted cochineal.

The value of different samples of cochineal may be compared by simply comparing the tints produced by fixed weights, dissolved in equal volumes of water, but more accurately by dissolving a given weight of powdered cochineal in water and observing how much of a standard neutralised alum solution is required to completely precipitate the colouring matter. There

is no really accurate method of estimating the colouring power.

Liebermann finds that the finest kinds of cochineal contain only about 10 p.c. of pure colouring matter. The percentage of colouring matter in ordinary cochineal was determined by precipitating the aqueous solution with lead acetate, purification of the lead compound, determination of the lead contained in it, and of the colouring matter by difference. Cochineal carmine is insoluble in alcohol, and nearly insoluble in water. An analysis of a very pure specimen gave the following results:

Water . . . . .	17 p.c.
Nitrogenous substances . . . . .	20 „
Colouring matter . . . . .	56 „
Ash . . . . .	7 „
Wax . . . . .	traces

The nitrogen, which amounts to about 3.7 p.c. on the dry carmine, is probably chiefly present as albuminous substances, since on fusion with potash a smell of indole is produced.

On heating the dry carmine to 180° it is converted into *ruficarmine*, and at a still higher temperature (250°) evolves CO<sub>2</sub>, apparently showing that the dyestuff is a carboxylic acid. Liebermann could obtain no confirmation of the statement that the dyestuff is a glucoside (S. C. I. 4, 585).

**COCHINEAL RED.** Syn. *Brilliant Ponceau*; v. AZO-COLOURING MATTERS.

**COCHINEAL SCARLET** v. AZO-COLOURING MATTERS.

**COCHINEAL WAX and FAT.** The wax is obtained by extracting the cochineal with benzene, and consists almost entirely of a substance to which Liebermann gives the name *coccerin*. After the removal of the coccerin the fat is extracted with ether; it consists of myristin and an oil containing fatty acids. The following are the percentages of coccerin in various samples of cochineal (extracted whole with benzene):

Silver cochineal . . . . .	1.0	p.c.
Mexican silver cochineal . . . . .	1.7	„
Teneriffe silver cochineal . . . . .	2.0	„
Zaccatille . . . . .	0.5	„
Teneriffe black cochineal . . . . .	0.7-1.0	„
Mexican black cochineal . . . . .	1.5	„
Granilla . . . . .	4.2	„

By powdering the cochineal before extraction the percentage increased by about one-half, except in the case of Granilla, where the granules are exceedingly small. The percentage of myristin is on the average about 1.5-2.0, and of fluid fat and fatty acids 4.0-6.0, so that the average total quantity of wax and fat contained in a silver cochineal is about 12 p.c. After recrystallising from benzene or acetic acid coccerin forms thin glistening plates of melting-point 106°. It is sparingly soluble in all cold solvents, and nearly insoluble in alcohol and ether. It has the constitution C<sub>30</sub>H<sub>40</sub>(C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>)<sub>2</sub>. On saponification with alcoholic potash it gives *cocceryl alcohol* C<sub>30</sub>H<sub>40</sub>(OH)<sub>2</sub> and *cocceric acid* C<sub>16</sub>H<sub>12</sub>O<sub>4</sub>. The alcohol forms a white crystalline powder of melting-point 101-104°. The acid melts at 93°, and is soluble in hot alcohol, benzene, &c.; its ethyl ether melts at about 70°. The myristin C<sub>14</sub>H<sub>22</sub>(OC<sub>11</sub>H<sub>21</sub>O)<sub>3</sub> forms colourless crystals of melting-point 55°, easily soluble in

warm alcohol &c.; on saponification it gave glycerol and myristic acid C<sub>14</sub>H<sub>22</sub>O<sub>2</sub> of melting-point 51° and boiling-point 215° at 100 mm. (S. C. I. 4, 585).

**COCINIC ACID** v. UMBELLIC ACID.

**COCOA.** The cocoa of commerce is made from the seeds of *Theobroma cacao*, nat. ord. *Euphorbiaceae*, a tree growing in the West Indies, Central America, Brazil, &c. It is also successfully cultivated in parts of Asia and Africa. The tree usually grows to a height of 12 to 20 feet, but is sometimes much higher. It begins to bear fruit when three years old, and attains full productiveness when seven or eight years old. The seeds are ovate, flattened, 0.7 to 0.9 inch long and .39 to .58 inch broad: they are covered with a thin red or grey-brown friable shell. The taste of the fresh seed is oily, bitter, and rather unpleasant. The seeds themselves are arranged in a fruit of 5 to 12 inches in length and about 3 inches in diameter, in which they are embedded in five rows, their number amounting to forty or upwards in a large specimen of Central American growth. In the West Indies and other places the fruit is smaller and contains fewer seeds. Being placed in bulk the seeds ferment; by which means much of their disagreeable, harsh flavour disappears and is replaced by an aromatic smell, whilst their colour becomes darker both then and during the subsequent drying which is performed in the sun or before a fire. Finally the beans are roasted after the manner of roasting coffee, and manufactured into cocoa bearing various names. Of these *cocoa nibs* are the bruised roasted beans deprived of their husky covering; *flake cocoa* is the nibs ground and formed into a coarse paste which is afterwards dried; *rock cocoa* is a similar preparation to which certain proportions of sugar or sugar and some starchy matters have been added. Most prepared cocoas consist of mixtures of cocoa, sugar, and starch in one form or another. Thus, in the case of Gibson v. Leifer, it was given in evidence that a commercial cocoa was compounded of 10 p.c. cocoa, 44 p.c. sugar, and 16 p.c. starch. There are, however, some preparations in which pure cocoa deprived of the greater part of its fat is offered to the public.

*Chocolate* is manufactured from cocoa by grinding it into a paste to which sugar and flavouring substances such as vanilla, cinnamon, &c. are added.

*Analysis of Trinidad cocoa nibs (B. II):—*

Moisture . . . . .	5.23
Fat . . . . .	50.44
Starch . . . . .	4.20
Albuminous matter soluble . . . . .	6.30
„ insoluble . . . . .	6.96
Astringent principle . . . . .	6.71
Gum . . . . .	2.17
Cellulose . . . . .	6.10
Alkaloids . . . . .	0.81
Cocoa red . . . . .	2.20
Indefinite organic matter insoluble . . . . .	5.80
Ash . . . . .	2.75

100.00

*Fat or cocoa-butter or oleum theobromæ.* This forms about one-half of the weight of the cocoa seed. It is a white solid, soluble in boiling



alcohol, from which it crystallises on cooling; it melts at about 30°C. and solidifies at 23°. At common temperatures it is brittle with a smooth and equal fracture.

*Starch* is not very abundant, and appears to have been over estimated by some analysts, Wanklyn, *e.g.*, stating the amount to be 10 p.c. and Muter 19 p.c.; Boussingault, on the other hand, found 2.4 and 2.5 p.c. of starch and glucose.

*Albumin* is present in the insoluble form, and is associated with cellulose in the portion of the nib left after continued boiling in water.

*Astringent principle.* This substance is of the nature of tannin, though differing from the tannin of tea and coffee. It rapidly changes during analysis to cocoa-red, which renders its quantitative estimation difficult. It is precipitated by subacetate of lead, and can be obtained after removal of the lead by sulphuretted hydrogen. It gives a green precipitate with ferric

chloride not unlike caffeic acid under similar treatment (Bell).

The principal alkaloid of cocoa is *theobromine*  $C_7H_5N_3O_2$ . It is found in nearly equal quantities in the husk and nib or kernel of the bean. Payen found 2.0 p.c., Mitscherlich 1.5 p.c., Wolfram as a mean of six analyses 1.56 p.c., Muter 0.9 p.c. (*vs. THEOBROMINE*).

*Cocoa-red* is not present in the fresh bean, but arises from the oxidation of the natural tannin of the seed. It consequently appears in different quantities in different cocoas. It has the character of a resin and exhibits variable degrees of solubility, probably coinciding with the extent of oxidation which it has undergone.

*Ash.* The ash of cocoa nibs is estimated at 3 to 5 p.c.; in the husk it is much higher. The amount soluble in water is remarkable.

The following table will serve to show the composition of several kinds of cocoa and of the ash:—

*Roasted beans after removal of the husk (Heisch).*

—	Husk	Fat	Nitrogen	Albuminoids	Ash	Ash soluble in water	Ash soluble in HCl	H <sub>2</sub> PO <sub>4</sub> in ash	Moisture	Starch, gum, cellulose, &c.
Caracas	13.8	48.4	1.76	11.14	3.95	2.15	1.80	1.54	4.32	32.19
Trinidad	15.5	49.4	1.76	11.14	2.80	0.90	1.90	0.93	3.84	32.82
Surinam	15.5	54.4	1.76	11.14	2.35	0.80	1.85	1.23	3.76	28.35
Guayaquil	11.5	49.8	2.06	13.03	2.50	1.75	1.75	1.87	4.11	30.47
Grenada	14.6	45.6	1.96	12.40	2.4	0.60	1.80	1.35	3.90	35.70
Bahia	9.6	50.3	1.17	7.40	2.60	0.90	1.70	1.26	4.40	35.30
Cuba	12.0	45.3	1.37	8.67	2.90	0.95	1.95	1.13	3.72	39.41
Para	8.5	54.0	2.00	12.66	3.05	1.40	1.65	1.00	3.96	26.33

*Analysis of the ash of cocoa nibs and husks (Bell).*

—	1 Guayaquil nibs	2 Surinam nibs	3 Grenada nibs	4 Finest Trinidad nibs	5 Finest Trinidad husks
Sand	—	—	—	—	5.12
Silica	0.15	—	—	—	2.87
Sodium Chloride	0.46	0.53	0.57	0.65	0.44
Soda Na <sub>2</sub> O	0.46	0.63	0.57	0.83	0.94
Potash K <sub>2</sub> O	23.35	28.00	27.64	29.30	37.89
Magnesia	19.18	20.66	19.81	18.23	13.04
Lime	3.24	4.38	4.53	6.51	7.30
Alumina	0.10	0.04	0.08	0.08	0.55
Protoxide of iron	0.21	0.38	0.15	0.10	0.63
Carbonic anhydride CO <sub>2</sub>	0.69	3.31	2.92	4.19	10.80
Sulphuric do. SO <sub>3</sub>	2.75	4.29	4.53	3.91	3.25
Phosphoric do. P <sub>2</sub> O <sub>5</sub>	49.39	37.78	39.20	36.20	17.17
	100.00	100.00	100.00	100.00	100.00

The following table shows the general composition of commercial cocoas:—

*Analysis of commercial cocoas (Bell).*

—	Prepared cocoa	Ice-land moss cocoa	Rock cocoa	Flake cocoa	Cocoa-tina	Chocolatine	Finest Trinidad nibs	Chocolat de Sante	Cocoa Extract
Moisture	4.95	5.47	2.58	5.49	3.52	4.40	2.60	1.44	5.76
Fat	24.91	16.86	22.76	28.24	23.98	29.60	51.77	22.08	29.50
Starch (added)	19.19	24.70	17.56	none	none	none	none	2.00	none
Sugar (cane)	23.03	29.23	32.20	none	none	none	none	61.21	none
Non-fatty cocoa	27.89	25.74	24.90	66.27	72.50	66.00	45.63	13.27	64.74
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Wigner examined the nitrogenous constituents of cocoa, and showed that even in the very best samples 21.5 p.c. of the nitrogenous matter present is in a non-coagulable form. Cocoa therefore ranks lower as an article of food than has often been supposed.

The importation of cocoa has increased rapidly of late years, the figures being:

1860 . . . . .	4,583,124 lbs.
1870 . . . . .	6,943,102 „
1880 . . . . .	10,566,159 „
1887 . . . . .	27,352,568 „

It is subject to an import duty of one penny per lb.

**COCOA NUT OIL** *v.* OILS.

**CODAMINE** *v.* VEGETO-ALKALOIDS.

**CODEÏNE** *v.* VEGETO-ALKALOIDS.

**CELESTIN** *v.* STRONTIUM.

**CÆLINE** or **CERULEAN BLUE** *v.* COBALT; also PIGMENTS.

**CÆRULEUM**, *Cæline*, *v.* COBALT.

**CÆRULEIN**, *Anthracene green*, *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

**CÆRULIGNOL**  $C_{10}H_{11}O_2$ . A colourless oil of a burning aromatic taste and a smell resembling creosote, obtained from beech tar. Boils at  $240-241^\circ$  sp.gr. 1.0564 at  $15^\circ$ . It is somewhat soluble in water, freely soluble in alcohol, ether, and acetic acid. It is coloured red by sulphuric acid, and dark brown by potash in contact with the air. In alcoholic solution it gives with barym hydrate a characteristic deep-blue colouration. Ferric chloride in alcoholic solution gives a green, in aqueous solution a deep-red colouration. Cærulignol is decomposed on treating with hydrochloric acid at  $145^\circ$ , according to the equation  $C_{10}H_{11}O_2 + HCl = C_6H_5O_2 + CH_3Cl$ .

**COFFEE.** The coffee-tree, *Coffea arabica* of Linnaeus, is a plant belonging to the natural order *Cinchonaceæ*, which embraces, according to Lindley and Paxton, two species, *C. arabica* and *C. paniculata*. Other botanists distinguish eight other species, *C. microcarpa*, *C. umbellata*, *C. acuminata*, *C. subsessilis*, *C. laurina*, *C. racemosa*, *C. Bengalensis*, and *C. Indica*. Some of these are probably only varieties. However this may be, three species distinct from each other are now grown:—(1) Arabian or Mocha coffee, having short upright branches with a brittle leaf and seeds usually single in the berries. (2) Jamaica coffee, bearing longer and more pliable branches, a tougher leaf, and seeds almost always double in the berries. (3) East India or Bengal coffee, of which the leaf is smaller than the Jamaica variety, and the berry very small. Trees growing wild in the Cingalese jungle attain a height of 14 to 18 feet; but under cultivation and subjected to systematic pruning, the plant rarely exceeds 6 to 9 feet. Within the tropics the coffee-tree succeeds best at 1,200 to 3,000 feet above the sea-level, but grows at the height of 6,000 feet. When the mean temperature is about  $70^\circ$ , it may be grown as far as Lat.  $36^\circ$  N. It is cultivated in the West Indies, Mexico, Central America, Brazil, and Cayenne; in Western Africa, Egypt, Mozambique, and Natal; in Arabia, India, Ceylon, Sumatra, Java, Bourbon, Celebes, and other parts of the Eastern Archipelago, Siam, Fiji, and the islands of the Pacific. At the present time half of the world's supply comes from Brazil.

The manner of forming plantations varies somewhat in different countries; as, for instance, the young plants may be reared in nurseries, whence they are transplanted to their permanent position, or they may be gathered out of the old plantations; the age at which this is done also varies, as in Brazil where the shrub is usually two years old on its removal, or as in the West Indies where it is planted out at six months. Fruit is produced in the fourth year, and continues to be gathered for several years.

The coffee-fruit consists of a saccharine and somewhat glutinous pulp containing the seeds, which are usually double, lying face to face, but sometimes occurring singly. The pulp is removed by water and fermentation. Each seed is inclosed in a membranous covering, technically termed 'parchment,' which is shred from the bean by rollers, and carried away by winnowing. Coffee-beans range in colour from greenish-grey to brown. The following table will indicate the variation in size:—

	No. of seeds in a measure holding 50 grammes of water
Fine brown Java . . . . .	187
Fine Mysore . . . . .	198
Fine Neilgherry . . . . .	203
Costa Rica . . . . .	203
Good ordinary Guatemala . . . . .	207
Good La Guayra . . . . .	210
Good average Santos . . . . .	213
Fine long-berry Mocha . . . . .	217
Good ordinary Java . . . . .	223
Fine Ceylon plantation . . . . .	225
Good average Rio . . . . .	236
Medium plantation (Ceylon) . . . . .	238
Manilla . . . . .	248
Ordinary Mocha . . . . .	270
West African . . . . .	313

Coffee undergoes important changes in the process of roasting, the object of which process is to develop its aroma and to destroy its toughness so that it may easily be reduced to powder. Great care is necessary to ensure an equable roasting of all the beans, and to attain the exact point at which torrefaction should cease. If, on the one hand, rawness is not removed, the flavour of the bean is not developed; on the other hand, if too much heat is permitted, a strong empyrenematic flavour is produced, which renders the coffee infusion nauseous.

The chemical composition of coffee has been investigated by many chemists with somewhat variable results. Schröder found that the raw beans distilled with water in a retort communicated to it their flavour, and rendered it turbid, whence they seemed to him to contain some volatile oil. On reboiling the beans, filtering, and evaporating the liquor to a syrup, adding alcohol till no more matter was precipitated, and then drying it, he found 17.58 of a transparent extract of a yellowish-brown colour, which constitutes the characteristic part of coffee, though it is not, in that state, the pure proximate principle called *caffeine* discovered by Runge in 1820 (*v.* CAFFEINE). The bean also contains a resin and a fatty substance resembling snet, tannic acid, and an acid which has been named *caffic* or *caffetannic* acid.

The following table shows the composition of raw coffee-beans from various districts:

*O. Lerxsis* (Ar. Ph. [3] 8, 294).

—	Gummy matter	Caffeine	Fat	Tannic and caffeitanic acid	Cellulose	Ash	Potash	Phosphoric acid
Finest Jamaica plantation	25.3	1.43	14.76	22.7	33.8	3.8	1.87	0.33
Finest green Mocha . . .	22.6	0.64	21.79	23.1	29.9	4.1	2.13	0.42
Ceylon plantation . . .	23.8	1.53	14.87	20.9	36.0	4.0	—	0.27
Washed Rio . . .	27.4	1.14	15.95	20.9	32.5	4.5	—	0.51
Costa Rica . . .	20.6	1.18	21.12	21.1	33.0	4.9	—	0.46
Malabar . . .	25.8	0.88	18.80	20.7	31.9	4.3	—	0.60
East Indian . . .	24.4	1.01	17.00	19.5	36.4	—	—	—

Commaille (Moniteur Scient. [3] 6, 779) found in undressed Mysore coffee:

Hygroscopic water (extremes of 24 determinations) . . .	6.3 to 15.7
Fatty matters . . .	12.68
Glucose . . .	2.60
Dextrin . . .	—
Legumin-casein . . .	1.52
Albumen . . .	1.04
Total quantity of caffeine . . .	0.42 to 1.31
Ash . . .	3.882
Coffee extract with cold water . . .	24.97
" " " warm water . . .	37.20
Coffee extract with alcohol of 60 p.c. . . . .	23.15

Roubiquet and Bontron (J. Ph. 23, 101) found in addition to fat, extractive matter, and caffeine, a white crystallisable substance, and an acid which was precipitated by acetate of lead.

The ash of the following parts of the Brazilian coffee-tree was analysed by H. Ludwig (Ar. Ph. [3] 1, 482), viz.:

- I. Root of a young tree in bearing.
- II. Root of an old tree.
- III. Leaves.
- IV. Pulp of the pericarp.
- V. Parchment-like coating of coffee-beans.
- VI. Coffee-beans grown on gneiss soil.
- VII. Coffee-beans grown on limestone soil.

—	I.	II.	III.	IV.	V.	VI.	VII.
K <sub>2</sub> O . . .	16.21	3.99	14.95	15.56	15.87	14.13	44.03
Na <sub>2</sub> O . . .	2.18	6.66	1.13	trace	5.10	5.84	5.85
CaO . . .	27.04	38.04	20.82	16.83	21.92	8.64	4.89
MgO . . .	4.15	5.39	7.96	5.63	4.62	8.14	8.01
Fe <sub>2</sub> O <sub>3</sub> . . .	3.39	5.03	3.58	11.38	7.12	16.54	1.96
Mn <sub>2</sub> O <sub>4</sub> . . .	0.44	trace	0.40	trace	—	trace	trace
Al <sub>2</sub> O <sub>3</sub> . . .	7.85	1.59	9.11	trace	4.19	2.78	trace
SiO <sub>2</sub> . . .	6.16	1.23	9.60	15.16	9.25	1.65	0.37
CO <sub>2</sub> . . .	27.55	25.16	21.03	20.13	13.28	8.34	21.24
P <sub>2</sub> O <sub>5</sub> . . .	2.28	11.30	6.23	9.99	16.70	18.65	10.54
SO <sub>3</sub> . . .	2.26	1.38	3.99	3.94	1.95	15.28	1.64
Cl . . .	1.05	0.25	1.56	1.34	trace	trace	0.98
I . . .	—	—	—	0.88	—	—	—
	100.59	100.02	100.36	100.84	100.00	99.99	99.51

From this table it appears that the phosphoric acid in young trees increases from the root to the fruit and its separate parts. The increased proportion of phosphoric acid in the roots of old as compared with those of young trees is very remarkable.

Graham, Stenhouse, and Campbell inferred that sodium compounds were absent in coffee-beans. This supposition is not confirmed by the above table, wherein a considerable quantity is shown to be present. Ludwig found that silica increased in amount from the root to the leaves and pulp, decreased in the parchment, and entirely disappeared in the bean. The influence of soil may be noted in columns VI. and VII.

*Roasted coffee.*—When roasted to a yellowish-brown, coffee loses, according to Cadet, 12½ p.c. of its weight, and is in that state difficult to grind. When roasted to a chestnut-brown it loses 18 p.c., and when it becomes entirely black, though not all carbonised, it has lost 23 p.c.

Schröder has analysed roasted coffee comparatively with raw coffee, and he found in the first 12½ p.c. of an extract of coffee soluble in water and alcohol, which possesses nearly the properties of the extract of raw coffee, although it has a deeper brown colour, and softens more readily in the air. He found also about 10.4 p.c. of a blackish-brown gum; 5.7 p.c. of an oxygenated extract, or, rather, *apothème*, soluble in alcohol, insoluble in water; 2 p.c. of a fatty matter and resin; 69 p.c. of burnt vegetable fibre, insoluble. On distilling roasted coffee with water, Schröder obtained a product which contained the aromatic principle of coffee; it reddened litmus paper and exhaled a strong and agreeable odour of roasted coffee. If coffee is roasted in a retort, the first portion of the aromatic principle condenses the yellow liquid in the receiver; and this may be added to the coffee roasted in the common way from which this matter has been expelled and dissipated in the air. Chenevix affirmed that by



the roasting of coffee a certain quantity of tannin possessing the property of precipitating gelatine is generated. Cadet made the same observation, and found, moreover, that the tannin was most abundant in the lightly roasted coffee, and that there was little of it in coffee highly roasted. Passé and Schröder, on the contrary, stated that solution of gelatine does not precipitate either the decoction of roasted coffee or the alcoholic extract of the coffee. Rungé could obtain no precipitate with gelatine; but he says that albumen precipitated from the decoction of roasted coffee the same kind of tannin as is precipitated from raw coffee by lead acetate (Ure).

Coffee is injured when roasted to such a degree as to lose 20 p.e. of its weight. Since the fine essential oil rapidly escapes after the bean is broken up, coffee should not be ground until required for infusion.

O. Bernheimer (W. A. B. [2 Abth.] 81, 1032-1042) found that during the roasting of coffee, water vapour is first given off, then suddenly an evolution of carbonic anhydride, and distillation of volatile substances commences. The distillate consists of an aqueous liquid and a solid part. The former contains caffeine, caffeol, acetic acid, quinol, methylamine, and acetone; the latter consists of fatty acids, chiefly palmitic. Pyrrol escapes during roasting. Of fatty acids 0.48 p.e. of the coffee employed was volatilised; of caffeine 0.18 p.e.; and of caffeol 0.05 p.e.

Bernheimer found that raw coffee beans (50 kg.) roasted in a revolving drum yielded a liquid distillate (5 l.), and a solid portion (680 g.) floating thereon. The uncondensable vapours contained carbonic anhydride, and, on passing them through dilute hydrochloric acid, a resinous body was deposited, having the appearance of pyrrol-red.

A. *Liquid distillate*.—The crude liquid distillate filtered from solid particles has a yellow colour and the fragrant odour of coffee. On agitating it with ether, and evaporating the ethereal extract over the water-bath, a dark heavy oil was obtained, smelling like coffee, and yielding, on redistillation, first a few drops of liquid having the odour of acetone, afterwards, for the most part, acetic acid and water. The thermometer then rose quickly to 200°, above which point there passed over an oil smelling like coffee, the temperature at the same time rising to 300°. Above this point there passed over a very small quantity of liquid, which immediately solidified to a mass, having the buttery aspect and rancid odour of the higher fatty acids. This portion, and the liquid which passed over from 200° to 300°, were neutralised with sodium carbonate, whereupon a thick dark coloured oil was thrown down, which was separated from the supernatant liquid by means of a tap-funnel, and washed with water rendered very slightly alkaline by potash.

The alkaline wash-waters contained no fatty acids, but, when acidulated with sulphuric acid and agitated with ether, they yielded a substance which, after evaporation of the ether, filled the liquid with a pulp of crystals, and after precipitation crystallised in colourless needles exhibiting the characters of *quinol* (m.p. 171°;

converted into quinhydrone by the action of ferric chloride).

The oil above mentioned, designated by Bernheimer as *cafféol*, was dried over calcium chloride and fractionally distilled, the greater part passing over from 195° to 197°. The distillate smells very strongly of coffee, is apparently insoluble in cold water, but imparts to it the characteristic odour; slightly soluble in hot water, very slightly in aqueous potash, very easily in alcohol and ether, the alcoholic solution giving, with ferric chloride, a red colouration, which does not disappear on addition of sodium carbonate. Analysis led to the formula  $C_{15}H_{10}O_2$ . Caffeol is oxidised by chromic acid mixture, without formation of any definite products. By fusion with potash it yields salicylic acid. The portion of the crude liquid distillate not taken up by ether, when concentrated over the water-bath, yielded groups of needle-shaped crystals, exhibiting the composition and properties of *caffeine*  $C_8H_{10}N_4O_2$  (0.28 p.e. of the coffee). The mother-liquor was found to contain *methylamine* and *trimethylamine*.

B. *Solid distillate*.—The black mass floating on the crude liquid distillate was found, by a preliminary examination, to consist of a mixture of the higher fatty acids. By saponification, and treatment of the product by Heintz's method of separation, this mixture yielded, as chief constituent, *palmitic acid* melting at 60°, and a very small quantity of another acid having a melting-point a few degrees higher than that of lauric acid.

*Detection of chicory in ground coffee*.—Chicory may generally be detected by sprinkling the ground mixture on cold water, when nearly the whole of the coffee floats whilst the chicory separates and sinks to the bottom, colouring the liquid brown. If examined under the microscope the sediment of chicory which reaches the bottom of the vessel will be found to exhibit the characteristic loose, large cells, with dotted vessels and branching lactiferous ducts. Even to the touch the difference is evident, for, whilst chicory under these conditions will feel soft and even, the coffee-grains remain hard and gritty.

A. Winter Blyth (Foods; their Composition and Analysis, 350) gives the following summary of the influence of chicory on the coffee mixture:—

(1) It decreases the gum, the latter seldom rising in chicory to more than 15 p.e., whilst in coffee it has not been found less than from 21 to 28 p.e.

(2) It increases in sugar, roasted coffee having seldom so much as 2 p.e. of sugar; whilst chicory when roasted has at least 8 or 9 p.e.

(3) It decreases the fatty matter, the fat of chicory ranging from 1 to over 2 p.e., that of coffee being about 14 to over 20 p.e.

(4) It decreases the tannic and caffeotannic acids, chicory being destitute of tannin.

(5) It decreases the caffeine, chicory possessing no alkaloid.

(6) It profoundly modifies the constitution of the ash, especially by introducing silica, which is not found to any great extent in coffee-ash.

Graham, Stenhouse, and Campbell laid stress upon the presence of silica as a means of detec-

tion of the admixture of chicory. Their analysis, showing the principal differences in the composition of the respective ashes, giving:

	In coffee ash.	In chicory ash.
Silica and sand . . . . .	—	10.69 to 35.85
Carbonic acid . . . . .	14.92	1.78 to 3.19
Sesquioxide of iron . . . . .	0.44 to 0.98	3.13 to 5.32
Chlorine . . . . .	0.26 to 1.11	3.28 to 4.93

According to F. M. Rimmington (Ph. J. Trans. [3] 11, 529), chicory and dandelion may be detected in coffee by treating it with bleaching-powder, after previous boiling with sodium carbonate and washing with water to remove extractive matter. By this means chicory and dandelion are bleached, whilst coffee undergoes little or no change.

The presence of leguminous seeds and cereals may be detected by boiling the sample with animal charcoal and water, filtering and testing for starch in the cold liquid with iodine. Neither coffee nor chicory contains starch. To determine to what vegetable the starch belongs recourse must be had to the microscope.

**COGNAC** *v.* BRANDY.

**COKE** *v.* FUEL.

**COLCHICINE** *v.* VEGETO-ALKALOIDS.

**COLCHICUM.** *Meadow saffron.* (*Colchique*, Fr.; *Herbstzeitlose*, Ger.) The corm or seeds of the *Colchicum autumnale* (Linn., Benth. A. T., 288). This plant is found in meadows and pastures throughout Europe, where its crocuss-like flowers, usually of a lilac hue, make their appearance in September and October.

Colchicum is a poisonous drug long known to medicine. It has been subject to repeated investigation with a view to isolate its active constituent or constituents. Among earlier inquiries are those of Melander and Moretti, 1810 (Bl. Ph. 2, 217); Stoltze, 1818 (B. J. 19, 107; 20, 135); Pelletier a. Caventou, 1820 (A. Ch. (2) 14, 69; J. Ph. 6, 364); Buchner, 1832 (R. P. 43, 376). Besides substances common to plants, such as starch, gum, cellulose, sugar, oil, resin, &c., the older workers detected a bitter extractive possessing physiological activity, and Pelletier and Caventou regarded it as containing gallate of veratrine. Geiger a. Hesse, in 1833 (A. 7, 274), showed, however, that the bitter alkaloidal compound, which they describe as crystalline, has properties quite distinct from veratrine, and they gave it the name *colchicine*. It is faintly alkaline, is sparingly soluble in water, but dissolves readily in alcohol and chloroform, the latter extracting it from its aqueous solution; the dry compound strikes a deep violet to blue colour with concentrated nitric acid, and its aqueous solution is precipitated brown by tincture of iodine, yellow by platinum chloride solution, and white by tannic acid. The corm yields less than 0.1 p.c. of colchicine. The subject is further studied by Aschoff (Ar. Ph. [3] 89, 4); Bley (Ar. Ph. [3] 89, 18); Hübschmann (Ar. Ph. [3] 92, 330); and Oberlin (A. Ch. [3] 1, 108). The last mentioned observer, by the action of dilute acids, succeeded in breaking colchicine up into a new alkaloid *colchicine* and other products. This compound was obtained in colourless laminae or needles sparingly soluble in cold, more so in boiling water, readily in alcohol and chloroform, in-

soluble in ether or benzene. Full directions for extracting colchicine from the crude drug, and its conversion into colchicine are given by Hertel (P. Z. 1881, 245), who observes that when exposed to the air colchicine gives off ammonia and water, and is converted successively into two resins: (a) *colchico-resin*  $C_{31}H_{60}N_2O_5$  (?), and (β) *colchico-resin*  $C_{31}H_{38}NO_{10}$  (?). These resins are formed in the official wine of colchicum, but are not indications of therapeutical deterioration, for they possess equal medicinal value with the alkaloid from which they are derived.

Important contributions to the chemistry of colchicine and colchicine have recently been made by Zeisel (M. 4, 162; 7, 557; 9, 1; 9, 865). After reviewing previous work, this observer assigns to *colchicine* the formula  $C_{22}H_{23}NO_6$ . It melts at about 145° and forms a characteristic crystalline compound with chloroform  $C_{22}H_{23}NO_6 \cdot 2CHCl_3$  (Houde, C. R. 98, 1442; Zeisel, C. R. 98, 1587). Colchicine is slightly basic, forming a *gold salt*  $(C_{22}H_{23}NO_6)HAuCl_4$ . *Methyl colchicine*  $C_{22}H_{23}MeNO_6$  has also been obtained. In the conversion of colchicine into *colchicine*  $CH_3OH$  is evolved, and the new alkaloid has the composition  $(C_{21}H_{23}NO_6)_2 \cdot H_2O$ . It melts at 139–141°, loses its water of crystallisation at 140–150°, becoming solid, and on further application of heat the anhydrous alkaloid softens at 161° and melts at 172°. Colchicine appears, therefore, to be a methylecolchicine. When colchicine is treated with concentrated hydrochloric acid the reaction does not stop with the formation of colchicine by the displacement of one methyl group; but this is accompanied by that of an acetyl radicle leaving an *acid*  $C_{19}H_{21}NO_6$  or  $(C_{18}H_{20}NO_3)COOH$ . In the further progress of the reaction this compound loses another methyl group giving rise to a second *acid*  $(C_{17}H_{18}NO_3)COOH$ , and finally by the displacement of two additional methyl groups colchicine *acid*  $(C_{15}H_{16}NO_3)COOH$  is obtained. The second acid described is therefore *dimethyl colchicine acid*, and the first acid *trimethyl colchicine acid*; while colchicine is regarded as *acetyl trimethyl colchicine acid* and colchicine, which does not possess acid properties, as the methyl ether of colchicine. Colchicine is basic, forming the *gold salt*  $C_{22}H_{23}NO_6 \cdot HAuCl_4$ , but it is also acid, or at least phenolic, giving rise to the *copper derivative*  $(C_{22}H_{23}NO_6)_2Cu \cdot 5H_2O$ . The acid property of colchicine is further apparent in the readiness with which it combines with alkalis. By treatment with methyl iodide and sodium methylate colchicine may be reconverted into colchicine.

Colchicum is a favourite remedy in the treatment of gout and rheumatism. It acts as an irritant of the alimentary canal and kidneys, being a purgative and diuretic, and in large doses these symptoms become more and more violent until a fatal result follows. The action is cumulative (Mairet a. Combemerle, C. R. 104, 439, 515). Post mortem examination of the stomach contents by treatment with alcohol, and purification of the extract obtained by fresh treatment with alcohol or with chloroform, and then the application of the nitric acid and other tests, may be adopted in cases where death is supposed to have been caused by colchicum. Cf. Daumenberg (Ar. Ph.

[3] 8, 411; 10, 97), and Van Geldern (Ar. Ph. [3] 9, 32).

Flückiger (Ph. [3] 7, 372) recommends the colour reactions which an alcoholic extract of colchicum corms gives with mineral acids as a delicate means of detecting those acids.

A. S.

**COLCOTHAR.** The reddish-brown residue of ferric oxide obtained in the manufacture of fuming oil of vitriol.

**COLLIDINE** *v.* BONE OIL.

**COLLODION** *v.* PHOTOGRAPHY.

**COLLOTYPE** *v.* PHOTOGRAPHY.

**COLOCYNTH.** *Bitter apple.* (*Coloquinte*, Fr.; *Koloquinthe*, Ger.)

The fruit, peeled, dried, and freed from seeds, of the *Citrullus Colocynthis* (Schrader) a climbing plant of the gourd family, inhabiting the warm dry districts of the Old World; India, Persia, Arabia, Syria, and the African and European shores of the Mediterranean. *Cf.* Benth. a. T. 114.

Colocynth was well known to Greek, Roman, and Arabian medicine, and in the form of solid extract enters into many of the purgative pills of modern pharmacy. It was chemically examined early in the century, amongst others by Vauquelin (J. Phys. 84, 338); Braconnot (J. Ph. 10, 416); Herberger (R. P. 35, 368); Bostick (Ph. 10, 289); and Meissner (Pereira, Mat. Med. 3rd ed. 2, 1737). It was, however, Walz in 1858 who first isolated an active constituent, *colocynthin*, from the drug (Ar. Ph. 96, 241; 99, 338; J. 1858, 531; 1861, 757). The alcoholic extract is treated with water, the aqueous solution precipitated by acetate and sub-acetate of lead, and the clear liquid thus obtained after being freed from lead by sulphuretted hydrogen is precipitated by tannic acid. The precipitate dissolved in alcohol is freed from tannic acid by treatment with basic acetate of lead, and the crude *colocynthin* thus obtained is finally purified by washing with ether. *Cf.* Lebourdais (A. Ch. [3] 24, 58) and Henke (Ar. Ph. 221, 200).

Colocynthin is a sticky mass, brittle when dry (Henke), is indistinctly crystalline (Walz). It has an intensely bitter taste, and acts as a drastic purgative. Walz assigns to it the formula  $C_{50}H_{81}O_{27}$ . Water and alcohol dissolve it, but it is insoluble in ether, chloroform, and most other solvents. Yield from the drug 0.6 p.c. (Henke). The aqueous extract reduces Fehling's solution. With concentrated acids *colocynthin* gives colour reactions: with sulphuric acid, deep red; nitric acid, bright red; hydrochloric acid, bright yellow. For other tests *v.* Johannson (Fr. 24, 154). According to Walz, *colocynthin* is a glucoside breaking up by treatment with dilute acids into glucose, and a resinous product *colocynthein*. The same observer obtained from the alcoholic extract of *colocynth* a crystalline substance, insoluble in water but soluble in ether, which he named *colocynthinin*.

It has been sometimes required to search for *colocynth* in beer *v.* Dragendorff (Ch. Centr. 1881, 285, 299).

A. S.

**COLOGNE YELLOW** *v.* CHROMIUM.

**COLOPHAN** *v.* OLEO-RESINS.

**COLOPHANTHRENES** *v.* RESINS.

**COLOPHENE CAMPHOR** *v.* CAMPHORS.

**COLOPHONY** *v.* RESINS.

**COLOPTENE** *v.* RESINS.

**COLORIMETERS, CHROMOMETERS, or CHROMATOMETERS.** These instruments, the use of which has very largely increased during recent years, are employed in quantitative analysis for determining the relative intensity of colour of substances either in solution or in the dry way.

A useful device introduced by Dupré (An. 5, 123) may be mentioned under this heading. In the volumetric estimation of silver with potassium chromate as an indicator, especially when the solution is weak, it is somewhat difficult, on account of the original yellow colour of the solution, to observe the first tinge of red produced by the formation of the silver chromate.

Dupré interposes, between the eye and the test liquid, a flat glass cell (of which the faces are about half an inch apart) containing a solution of potassium chromate of such strength as will neutralise the colour of the test liquid, which thus appears perfectly colourless, and in which the faintest appearance of red is readily visible. The cell filled with other liquid may be similarly adopted in many other titrations.

A useful colorimeter for general purposes, devised by Mills, is shown in fig. 1. It consists of a glass jar closed above by a cap of which the length is sufficient to cover the top of the liquid. The cap is perforated in the middle and carries a short tube in which slides a glass rod bent as shown, and supporting, exactly at right angles to the axis of the jar, a flat circular opaque white disc. In the bottom of the jar are laid, one above another, a red and a green glass disc which form a

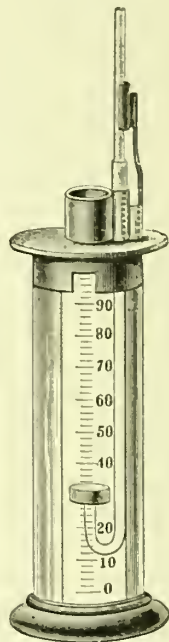


FIG. 1.

black background to the white disc. When examining solutions of certain colours, a background of a colour other than black may be advantageous, and the white disc itself may be covered by a coloured plate. The white disc is lowered to the bottom of the jar by moving its rod, and the jar is filled to exactly 100 divisions with a standard liquid. The standard used may be of the same composition as the liquid under examination, or may be made of any suitable materials, but its colour must be identical in quality with that of the liquid tested, and its value per unit volume in terms of the substance estimated must be accurately known. Thus, the permanent standards used in the estimation of combined carbon in steel are generally made of mixed solutions of *metallic salts*, and in the estimation of ammonia in water a solution coloured with *caramel* and a little *aniline red* has been used (Leeds, C. N. 37, 229).



The white disc is raised until, on looking vertically down through the liquid at the disc, the depth of tint appears suitable. A second apparatus is then filled to 100 divisions with the liquid to be tested, and its disc is adjusted until the colours of the columns of liquid in the two jars appear of equal intensity. The lengths of these columns are noted, and the comparison is repeated, using, preferably, a different length of column of the standard.

The relative strength of the solutions varies *inversely* as the lengths of the columns, so that if 1 c.c. of the standard solution correspond with  $x$  parts by weight of the substance estimated, the weight of that substance in 1 c.c. of the test solution will be

$$\frac{\text{length of column of standard solution} \times x}{\text{length of column of test solution.}}$$

If the strength of the standard differ by more than 10 p.c. from that of the test liquid, it is advisable to dilute one or other before comparison.

By placing on the white disc a small, black, hemispherical button, this instrument may be used for determining the strength of turbid solutions, such as milk, or for ascertaining the amount of a precipitate suspended in a liquid. Milk is diluted before examination with 99 parts of water, and is compared with a similarly diluted milk of known strength, the disc with the button being adjusted in each tube as above until just invisible.

For the examination of precipitates, a solution of considerable suspensory power is prepared by dissolving 100 grams of gelatine, 100 grams glacial acetic acid, and 1 gram of salicylic acid (to prevent decomposition of the gelatine by keeping) in 1 litre of distilled water.

The solution is clarified with white of egg and filtered hot. For estimation of sulphuric acid, this solution is charged with barium chloride, and is added to a weak standard solution of sulphuric acid or a sulphate, and to the solution to be tested, the two turbid liquids being then compared as above. By the use of other reagents, lime, zinc, and a large number of other substances may be estimated. The slight alteration in the level of the liquid caused by the varying length of the sliding tube contained in the liquid when adjusting the height of the white disc is found by experiment, and a correction must be introduced into the calculation for variations of more than two or three divisions. A very useful colorimeter, especially designed for the estimation of carbon in steel, but of course available for other purposes, has been introduced by Stead (Proc. Iron and Steel Inst. 1883, No. 1, 213). A similar, but more convenient apparatus, devised by Ridsdale (S. C. I. 1886, 586) is shown in fig. 2. Three glass tubes, each fitted below with a small, opaque, white cylinder, are placed beneath a movable mirror, in a stand which may be turned to any position upon its weighted base. The central tube is removable and is closed below, the outer tubes are drawn out and pass through india-rubber corks into ruby glass bottles, containing standard solutions of different strengths. Each bottle has a tube with a stopcock through which the liquid may be introduced or removed,

and each is connected by a flexible tube with a syringe.

The liquid under examination is introduced into the central tube, and by working the syringes the standard solutions are raised in their tubes until the intensity of colour in each tube, as seen by looking into the mirror which is adjusted to reflect the light passing upwards through the tubes, is identical. Two distinct

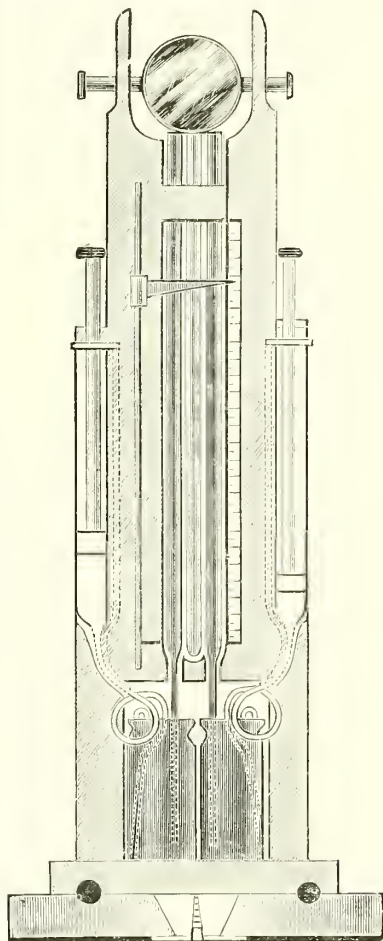


FIG. 2.

comparisons are thus simultaneously made, and, by noting the height of each column by means of the sliding pointer, the strength of the tested liquid may be ascertained from the formula already given. A very important advantage of this apparatus is that every part except the central tube is cleansed and re-charged without disconnection.

Ridsdale (S. C. I. 1888, 70) has devised an apparatus which serves for the examination of liquids of deeper tint than are available in the foregoing apparatus. The inner tube (fig. 3) is sealed below, the side tubes are perforated at the bottom. Each tube contains a loose white opaque plug, and each is held at any height by

a movable jaw pressed against it by an india-rubber band.

The centre tube is charged with, say, 10 divisions of the standard solution, and the test liquid is run into one of the side tubes, whence

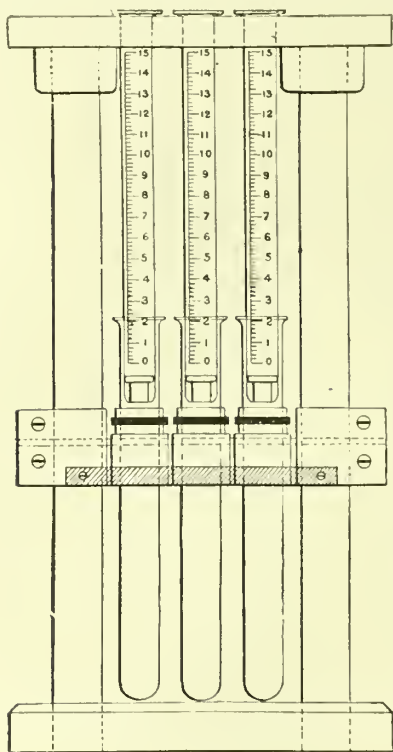


Fig. 3.

it passes at once into the lower tube. When this is nearly filled, it is gradually raised to bring a portion of its contents into the upper tube, until, on looking down vertically, the colours in the upper side tube and in the standard tube are of identical intensity. The calculation is made as already described. The lower tube beneath the standard tube must be raised with that of the side tube in order to equalise the effect of the double thickness of glass. When the solutions to be tested differ widely in tint, the standard tube may be perforated so that the length of its column may be readily adjusted.

Another arrangement in which the standard liquid is forced into a graduated tube from a reservoir is described by Günsberg (D. P. J. 228, 457).

The Nesslerising tubes adopted by Hehner (C. N. 33, 185) and recommended by Milne (S. C. I. 1887, 33) are two cylinders of equal and perfectly uniform diameter, holding about 100 c.c. Each is graduated from below, and at about the 30 c.c. division has a glass stopcock.

The two cylinders are placed side by side on white paper, and to one of them is added 100 c.c. of the liquid to be tested, followed by 2 c.c. of

Nessler's solution. To the other tube a suitable and known amount of standard solution of ammonium chloride is added, and the volume is made up to 100 c.c. with distilled water, after which 2 c.c. of Nessler's solution is added. The two liquids are looked at *vertically*, and the darker is allowed to slowly run off into a clean beaker, until their colours are equal. The comparison may be repeated after filling up from the beaker. The mode of calculation is the same as in former cases.

In a colorimeter devised by Leeds (C. N. 37, 229) comparison tubes are arranged in a rack, light being reflected through them by an inclined upper mirror, and again reflected to the eye of the observer from a mirror similarly placed beneath them. The standard liquid is contained in a bottle prism which is moved beneath one of the comparison tubes containing distilled water only, until the colour observed is identical with that in the tube containing the test liquid. The strength of the test liquid is calculated from the thickness of liquid in that section of the prism which is interposed.

An ingenious instrument, introduced by Mr. J. W. Lovibond, for the examination of liquids, powders, fabrics, &c., and known as the *tintometer*, is shown, partly in section, in fig. 4. It consists of a box, closed at one end by a ground

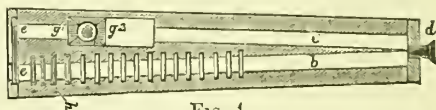


Fig. 4.

glass plate *e*, and separated into two divisions *b c*. The box is carried by a stand, adjustable to any angle. A square glass cell, of known width, along the line *g'g'*, containing the solution to be examined, is placed in one division, and glass plates *h* of similar colour (or, if necessary, of different colours, producing the proper tint in combination), and of known intensity, are placed in grooves in the other division, until, on looking through both tubes simultaneously through a single eye-piece *d*, shaded to prevent access of side light to the eye, the appearance through the glass plates is identical with that through the solution.

The standard plates are specially prepared of various colours, and each is distinguished by a number indicating its *colour* and another number showing the *intensity* of colour, *i.e.* the number of plates of that colour of unit intensity required to produce an intensity equal to that of the plate. The unit chosen by the inventor for each colour is an arbitrary one, but its actual value can be ascertained at any time by comparison with a standard solution of similar colour.

In some cases the glass plate *e* is wanting, and an adjustable plane glass mirror is used to reflect the light to the apparatus.

When the colour of a fabric is to be estimated the fabric is stretched on a block placed in the division *c*, and a white fabric of *similar texture*, previously compared with a plate of pure *plaster of Paris*, is placed in the division *b*. The standard plates are then inserted as above until the

appearances through the eye-piece are identical. *Powders, sugars, &c.*, pressed in a small tray placed in the division *c*, may be similarly examined, a tray containing pure plaster of Paris being placed in the division *b*.

For very delicate observations the intensity of the light used may be found and noted, before commencing, by closing the division *c* and placing in the divisions *b* as many standard plates of *neutral tint* as serve to obstruct all the light.

For further information *v.* Blue Books of H.M. Patent Office, A.D. 1886, No. 12,867; S. C. I. 1887, 522, 628, and 1888, 69.

Andrieux (C. R. 103, 281) describes an apparatus in which the *quality* and *intensity* of a colour are determined by comparison with a ray of polarised light.

König (Proc. Amer. Phil. Soc. [18] 7, 29, 184, 208, 211) has devised a method for estimating metals by the intensity of the colour imparted by them to the borax bead. He dissolves a known weight of the oxide in a known weight of borax, grinds the bead until its faces are flat, coats it with Canada balsam to render its rough faces transparent, and places it in an apparatus where it is viewed by a lens of small power, while, by means of a rack, a glass prism whose colour is complementary to that under examination, is moved before it until such a thickness is interposed that the colour of the bead is extinguished.

A photochemical process for estimating differences in the intensity of a colour has been described by E. J. Mills and Buchanan (S. C. I. 1888, 309). It has been applied to the comparison of dyed goods. A number of discs of the tissues are photographed on one negative from which a number of positives on paper sensitised with silver, are copied. These are treated as usual, soaked for a considerable time in sodium thiosulphate to remove the whole of the unaltered silver salt, well washed, and dried. The disc photographs of each tissue are cut from a number of positives and each set is burned separately. The silver in the residue is dissolved and estimated volumetrically. The relative amount of silver found in the different sets of discs directly represents the relative intensity of the colours.

The following colorimetric process for the estimation of minute quantities of sulphur in iron, mineral waters, black ash, slag, &c., is due to Wiborgh (C. Z. 10, 92; C. N. 1886, 54, 158).

The divided metal, ore, &c., or the concentrated solution, is introduced into a small flask provided with an india-rubber cork, through which passes a stoppered funnel for introduction of acid, and a narrow-mouthed funnel ground at the top. A disc of white calico, which has been previously saturated with a solution of 5 grams crystallised *cadmium nitrate* (or, preferably, *cadmium acetate*) in 100 c.c. of water and dried in a horizontal position on a cloth, is fixed between two india-rubber rings of the same interior diameters as the standard discs hereafter described, and the rings are firmly clamped over the funnel mouth. Dilute sulphuric acid is poured into the flask and heat is applied. In from 30 to 45 minutes the whole of the sulphur which is capable of conversion into sulphuretted hydrogen has passed off in that form and has

been *wholly* absorbed by the cadmium salt on the calico. The disc is removed and compared with a set of standard discs, similarly prepared from iron containing a known amount of sulphur. The standard discs should not be exposed too freely to light. Arsenic, carbon, silicon, and copper do not appear to affect the determination. This method is so delicate that a disc will show a tinge of the yellow colour due to the cadmium sulphide when so small a quantity as the 1000th of a milligram of sulphur is present per square centimetre. Other metals which give coloured sulphides may be used, but cadmium appears to be most generally satisfactory.

**COLOURS, DETECTION OF, ON DYED FABRICS.** Most colouring matters exhibit characteristic colour reactions when treated with various reagents. The reaction varies slightly according to the condition in which the colouring matter is examined, *i.e.*, in the free state, or applied to this or that fibre, &c.

The annexed tables show the reactions obtained on wool dyed with the several colouring matters named, when treated with a few simple reagents, such as are readily available to the dyer. The reagents required are: sulphuric acid 1·84 sp.gr.; hydrochloric acid 1·14 sp.gr.; sodium hydrate 10 p.c. solution; ammonia solution 0·880 sp.gr.; a solution containing equal weights of concentrated hydrochloric acid and stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ); 95 p.c. alcohol.

Small portions of the fabric should be steeped in porcelain basins containing a little of the reagent. Other portions should be gently warmed with the reagent in a test tube. It is always desirable to confirm the test by making a comparative experiment with material specially dyed with the suspected colouring matter.<sup>1</sup>

The following abbreviations are adopted in the tables:—M. L. & B. (Meister, Lucius, and Brüning); B. A. & S. F. (Badische Anilin and Soda Fabrik).

**COLUMBA** or **COLUMBO**; **COLUMBIC ACID** and **COLUMBIN** *v.* **CALUMBA**.

**COLUMBITE** *v.* **CERIUM METALS**.

**COLZA OIL** *v.* **OILS**.

**COMENAMINIC ACID** *v.* **BONE OIL**.

**COMMON CAMPHOR** *v.* **CAMPHORS**.

**CONCRETE** *v.* **CEMENTS**.

**CONDY'S FLUID** *v.* **MANGANESE**.

**CONESSINE** *v.* **VEGETO-ALKALOIDS**.

**CONGO** *v.* **AZO-COLOURING MATTERS**.

**CONGO, BRILLIANT**, *v.* **AZO-COLOURING MATTERS**.

**CONGO CORINTH** *v.* **AZO-COLOURING MATTERS**.

**CONGO RED** *v.* **AZO-COLOURING MATTERS**.

**CONGO YELLOW** *v.* **AZO-COLOURING MATTERS**.

**CONIFERIN** *v.* **GLUCOSIDES**.

**CONIMA RESIN** *v.* **OLEO-RESINS**.

**CONIMENE** *v.* **OLEO-RESINS**.

**CONINE** *v.* **VEGETO-ALKALOIDS**.

**CONQUINAMINE** *v.* **VEGETO-ALKALOIDS**.

**CONVOLVULIN** *v.* **GLUCOSIDES**; also **GUM RESINS**.

**COPAIBA, BALSAM OF** *v.* **OLEO-RESINS**.

**COPAIVA OIL** *v.* **OILS ESSENTIAL**; also **OLEO-RESINS**.

<sup>1</sup> Cf. J. J. Hummel's *Dyeing of Textile Fabrics* (Casell & Co., 1885), chapter xxvi. Also, R. Lepetit, S. C. I. 7, 773.



## RED COLOURS.

Colouring matter	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH	NH <sub>4</sub> OH	SuCl <sub>2</sub> + HCl	Alcohol	Other tests
Scarlet 2 R. (M. L. & B.)	Fibre not changed by cold HCl, but on boiling nearly decolourised and much colour extracted.	Dilute H <sub>2</sub> SO <sub>4</sub> no action. Concentrated H <sub>2</sub> SO <sub>4</sub> extracts the colour.	Nearly decolourised.	Fibre paler.	Fibre decolourised.	Little or no action.	HNO <sub>3</sub> gives violet spot which afterwards changes to bright yellow.
Scarlet 3 R. (M. L. & B.)	Fibre not changed even on boiling. Reddish-liquid extracted.	No action.	Nearly decolourised.	Little effect.	Fibre decolourised.	Little or no action.	HNO <sub>3</sub> , as with Scarlet 2R.
Patent Fast red (B. A. & S. F.)	Bluish-red liquid extracted. Fibre blackened, liquid slightly tinged red.	Fibre violet, liquid colourless, but on standing bluish-violet.	Fibre made paler, and red colour extracted.	No action.	Fibre decolourised (resists this test better than other scarlets).	Little or no action.	HNO <sub>3</sub> acts as with Crocein scarlet 7 B.
Cherry red B. (M. L. & B.)	Fibre little changed, liquid reddish-violet.	Fibre at first violet, finally blue. Liquid at first colourless, afterwards bright blue.	Fibre orange-red solution yellowish-red.	No action.	On heating, fibre becomes almost colourless, or pale lilac.	Little or no action.	HNO <sub>3</sub> gives a violet spot which afterwards becomes brownish with a faint blue border. It is not affected so readily by HNO <sub>3</sub> as the other red scarlets are.
Carmoisin (Fr. Bayer & Co.)	Dil. HCl: No action. Conc. HCl: Fibre dark reddish-violet, liquid slightly lilac. On washing the original colour is restored.	Fibre violet-black, liquid ditto.	Fibre somewhat brown, liquid bright pink.	Fibre unchanged, liquid pink.	Slight action in cold; on boiling fibre completely decolourised.	No action.	HNO <sub>3</sub> : Brown-violet. Disappears on washing.
Biebrich scarlet (Kalle & Co.)	Fibre violet, liquid colourless. On standing, liquid becomes greenish-blue.	Fibre and solution green.	Fibre dark bluish-red, liquid colourless.	No action.	Fibre decolourised.	Little or no action.	HNO <sub>3</sub> gives at first a dark-blue spot which changes to brown with a dark-blue border.
Orselline B.B. (Fr. Bayer & Co.)	Fibre at first violet-black, then black; solution pale indigo blue.	Fibre blue-black, liquid indigo blue, upon diluting becomes a reddish-violet.	Fibre violet, liquid reddish-violet.	Like NaOH.	Fibre slowly decolourised in the cold, rapidly upon boiling.	No action.	HNO <sub>3</sub> : Violet spots, which disappear on washing.
Crocein scarlet 7 B (Fr. Bayer & Co.)	Fibre at first violet, liquid colourless. On standing, fibre becomes blue, liquid greenish-blue.	Concentrated acid, fibre, and solution blue.	Colour of fibre blue.	—	Fibre decolourised.	Little or no action.	HNO <sub>3</sub> gives at first a dark-blue spot which changes to bright yellow with a greenish-blue border.
Azarine S (M. L. & Fr.)	Fibre gradually dark brown-red, liquid scarcely coloured. On diluting the original colour of the fibre is restored.	Fibre darker, liquid beautiful red. On diluting fibre and liquid become yellow.	Fibre bluish-red, solution bright cherry-red.	Action similar, but less marked than with NaOH.	On boiling the fibre and liquid become yellow.	Liquid coloured pale pink.	Pierle acid: Fibre brown. The material or yarn smells strongly of Turkey-red oil, and its ash contains the HNO <sub>3</sub> . No action. HNO <sub>3</sub> : Orange-red spot. On adding NH <sub>3</sub> to the yellow solution obtained with SuCl <sub>2</sub> and HCl, the fibre and liquid become violet.
Azoecine (Fr. Bayer & Co.)	Fibre dark red-violet, liquid pale lilac. On diluting the original colour is restored.	As with HCl.	Fibre dirty orange brown-red.	Fibre, scarlet-red, liquid scarcely coloured.	In the cold only very slight action; on heating the fibre is incompletely decolourised, liquid colourless.	No action.	HNO <sub>3</sub> : Brown spot, disappears on washing.
Primaline red (Brook, Johnson & Co.)	Fibre dark red-brown, liquid pale red-brown.	Fibre violet-black, liquid dirty dark violet. On diluting red.	Fibre dirty dark brown-red.	No action.	Fibre gradually changed to bright red-brown.	No action.	HNO <sub>3</sub> : No action. (This colouring matter is sold by R. Geigy as Poly-chromin.)
Congo (Fr. Bayer & Co.)	Dil. HCl: Fibre black. Conc. HCl: Fibre black.	Fibre black, liquid dark blue; on diluting remains blue.	Fibre much redder; liquid colourless; on washing, the original colour is restored.	Fibre becomes redder, liquid slightly pink.	Fibre at first black, then blue-grey, and finally deco-coloured.	Liquid a pale pink.	HNO <sub>3</sub> : Fibre dark blue-black; washing with NH <sub>3</sub> , the fibre becomes dark magenta-red.

Congo red (Berlin Aniline Co.)	Dil. HCl : Fibre immediately becomes blue-black. Conc. HCl : Fibre blue-black, liquid colourless.	Fibre blue-black; on shaking up dissolves with a dark-blue colour; on dilution remains blue-black.	Fibre scarcely changing, liquid colourless.	No action	Fibre at first blue-black, then blue, afterwards grey, at last decolourised, all in the cold.	No action	HNO <sub>3</sub> : Blue-black spot; NH <sub>3</sub> restores original colour. HNO <sub>3</sub> : Fibre reddish-brown; original colour is not restored by NH <sub>3</sub> , but the fibre is turned brownish-purple and the liquid bluish-red.
Delta purpurine G (Fr. Bayer & Co.)	Dil. HCl : Fibre brown-red liquid colourless. Conc. HCl : Fibre dirty greenish-black.	Fibre blue-black; liquid dark blue; on diluting at first grey, then reddish-brown.	No action	No action	Fibre at first dark brown, then brighter, then pink-red, finally decolourised.	No action	HNO <sub>3</sub> : Fibre violet-black, turned violet-red with NH <sub>3</sub> . Picric acid : Fibre brown-red.
Brilliant Congo (Fr. Bayer & Co.)	Dil. HCl : Fibre brown-red, liquid colourless. Conc. HCl : Fibre violet-black.	Fibre blue-black; liquid blue, on diluting purple-violet.	No action	No action	Fibre at first reddish-brown, then decolourised.	Slight extraction of colour.	HNO <sub>3</sub> : Fibre black, turned violet-black by NH <sub>3</sub> . Picric acid : Fibre brownish.
Benzopurpurine 1 B (Fr. Bayer & Co.)	Dil. HCl : Fibre red-brown, liquid colourless. Conc. HCl : Fibre dark brown.	Fibre blue-black, liquid blue-black, then violet.	No action	No action	Fibre at first brown-red, then pink, finally decolourised.	Slight extraction of colour.	HNO <sub>3</sub> : Fibre brownish-black. Picric acid : Fibre red-brown.
Benzopurpurine 2 B (Fr. Bayer & Co.)	Dil. HCl : Fibre bluish-black liquid colourless. Conc. HCl : Fibre blue-black.	Fibre blue-black; liquid dark blue, on diluting blue.	No action	No action	Fibre at first brown-red, then pink, finally decolourised.	Slight extraction of colour.	HNO <sub>3</sub> : Fibre brownish-black. Picric acid : Fibre red-brown.
Direct red (R. Geigy & Co.)	Dil. HCl : Fibre violet-black. Conc. HCl : Fibre blue, liquid colourless.	Fibre blue-black; liquid violet-black, on diluting greyish-blue.	Fibre darker and somewhat bluer; liquid brown-red.	Fibre beautiful fiery-red; liquid faintly reddish.	Fibre at first blue-black, then clear grey, finally decolourised.	No action	Remark.—All these colouring matters which are unaffected by NaOH are strongly attacked by hot soap solution and extracted.
Delta purpurine 5 B (Fr. Bayer & Co.)	Dil. HCl : Fibre red-brown. Conc. HCl : Fibre olive-black.	Fibre dark olive-brown colour; liquid dirty brown.	No action	No action	Fibre at first blue-black, then clear grey, finally decolourised.	No action	NHNO <sub>3</sub> : Fibre brownish-black, then more violet. Picric acid : Fibre dark brown.
Naphthalene red. (B. A. & S. F.)	Fibre dark green-black	Fibre blue-black, liquid blue-black.	Scarcely any action.	Slightly extracts the colouring matter without changing the colour of the material.	Fibre at first cinnamon brown, then gradually decolourised in the cold.	Some colour extracted.	HNO <sub>3</sub> : Fibre red-brown, unchanged by NH <sub>3</sub> . Picric acid : brown spot.
Rosazurine B (Fr. Bayer & Co.)	Dil. HCl : Fibre dark purple-red. Conc. HCl : Fibre olive-green.	Fibre dark blue; liquid dark blue; on diluting at first greenish, then red-violet.	No action	No action	Fibre at first dark purple-red, then decolourised.	Extracts some colouring matter with magenta-red colour.	HNO <sub>3</sub> : Fibre dark yellowish-grey, on washing and moistening with NH <sub>3</sub> red-brown.
Hessian purple N (Leonhardt & Co.)	Dil. HCl : Fibre black, liquid colourless.	Fibre black; liquid blue; on diluting grey-blue.	No action	No action	Fibre at first black, then decolourised.	Liquid scarcely coloured.	HNO <sub>3</sub> : Fibre violet-black, changed by NH <sub>3</sub> to dark red-brown.
Hessian purple B (Leonhardt & Co.)	Conc. HCl : Fibre dark grey, almost black.	Fibre grey-black, liquid pale blue.	No action; liquid pale pink.	Liquid pale pink.	Fibre at first reddish-grey, then decolourised.	No action	HNO <sub>3</sub> : Fibre dark purple-violet, with NH <sub>3</sub> dark brown.
Magenta	Fibre and solution yellow, colour restored on washing.	As with HCl	Fibre at first paler, afterwards nearly colourless, especially on heating.	Fibre decolourised.	Almost entirely decolourised on boiling; colour partly restored on washing.	A bluish-red liquid readily extracted.	Sodium sulphide decolourises. Magenta may be distinguished from archil and aurine as follows: Amyl alcohol extracts a bluish-red colour from material dyed with magenta. Amyl alcohol extracts a yellow colour from material dyed with aurine. Amyl alcohol extracts a pink or violet colour from material dyed with archil.

## RED COLOURS—continued.

Colouring matter	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH	NH <sub>4</sub> OH	SnCl <sub>4</sub> + HCl	Alcohol	Other tests
Acid magenta. (B. A. & S. F.)	Faint bluish-red liquid extracted, colour of fibre unchanged.	As with HCl . . .	Fibre decolourised in the cold.	Fibre decolourised, colour gradually restored on exposure to air.	Colour largely extracted on boiling.	Very little colour extracted.	To the alcoholic extract add NH <sub>4</sub> OH, magenta is decolourised. To the alcoholic extract add NH <sub>4</sub> OH, aurin turns bluish-red. To the alcoholic extract add NH <sub>4</sub> OH, archil remains unchanged.
Aurin . . .	Fibre yellow . . .	As with HCl . . .	Solution bright red.	As with NaOH . . .	In the cold, solution yellow.	Colour extracted.	—
Eosin A. (B. A. & S. F.)	Fibre pale yellow . . .	Fibre at once bright yellow.	Fibre yellow, liquid pink, fluorescent.	Fibre yellow, liquid yellow, fluorescent.	Fibre orange-yellow, solution pale yellow.	Soluble eosines not extracted if well dyed.	Hot water containing a little NH <sub>4</sub> OH gives a pink solution with soluble eosines. Boiled with concentrated KHO (20-40 p.c.), eosin G gives orange-red solution, which on continued boiling becomes purple, and finally blue with strong green fluorescence. Colour and fluorescence unchanged on dilution. Eosin B, boiled with KHO gives bluish-violet solution with pale green fluorescence. On dilution, liquid becomes reddish-purple. Eosin BX, boiled with KHO gives eventually olive-green solution without fluorescence.
Methyl-eosin . . .	Fibre yellow . . .	Fibre yellow . . .	Fibre pink, liquid pink, fluorescent.	As with NaOH . . .	—	Pink fluorescent solution.	—
Erythrosin, I. (B. A. & S. F.)	Fibre brownish-yellow . . .	Fibre yellow . . .	Fibre and liquid pink.	As with NaOH . . .	Fibre orange on boiling.	—	—
Phloxin, J. (P. Monnet & Co.)	Fibre yellow . . .	Fibre yellow . . .	Fibre and liquid pink.	Fibre and liquid pink.	Fibre yellowish on boiling.	—	—
Rhodamine . . .	Fibre dirty brick-red, liquid colourless. On washing the original colour is restored.	As with HCl . . .	Fibre somewhat darker and bluer, liquid colourless.	Fibre as with NaOH, liquid slightly pink and fluorescent.	In the cold no action. On heating fibre dirty brown-red, liquid slightly pink.	Slightly extracted, forming fluorescent solution.	HNO <sub>3</sub> : No action. HNO <sub>3</sub> : Orange-red spot, disappearing on washing. Rhodamine stands boiling with soap very well.
(B. A. & S. F.)				No action . . .	Fibre oranges-yellow, liquid bright yellow.	No action . . .	Gives no fluorescent solution on boiling with Al <sub>2</sub> (SO <sub>4</sub> ) (distillation in moulder and purifier). Bleaching powder and chromic acid bleach it. Boiled with Ba(OH) <sub>2</sub> solution, fibre becomes violet, HNO <sub>3</sub> gives a yellow spot.
Alizarin (with aluminina mordant)	Dilute, no action; concentrated, fibre bright yellow, liquid amber yellow.	Dilute, no action; concentrated, red colour extracted.	Fibre and solution violet.	No action . . .	—	—	An alkaline solution of K <sub>2</sub> FeC <sub>6</sub> has no action, nor has KMnO <sub>4</sub> . HNO <sub>3</sub> vapour converts it into yellow ultramarine. On heating, alizarin red loses brilliancy and becomes brownish, but retains most of the brilliancy on exposure to air. The ammoniacal, aqueous, or alcoholic solution give characteristic absorption spectra.



Purpurin (with almina mordant)	Boiled with dilute HCl fibre orange-yellow and liquid yellow.	As with HCl	Heated with dilute NaOH, fibre and liquid cherry-red.	Boiled with dilute NH <sub>4</sub> OH liquid and pale pink, fibre not changed.	Fibre brownish-red, liquid amber-yellow.	Solution red	HNO <sub>3</sub> gives a bright yellow spot. Bleaching powder bleaches it. Ba(OH) <sub>2</sub> turns fibre cherry-red and gives a pale bluish-red solution. Boiling with a solution of aluminium sulphate and cooling, gives an orange fluorescent solution. The yellow colour with SnCl <sub>2</sub> and HCl is turned a beautiful violet with NaOH.
Alizarin S (with almina mordant)	Fibre orange-brown, liquid orange. On diluting yellow.	Fibre orange-brown, liquid orange. On diluting yellow.	Fibre and solution violet.	Fibre beautiful dark red, liquid colourless.	Fibre gradually becomes orange, liquid yellow (in the cold). Decolourised on heating, liquid colourless.	No action	—
Safranline (Brook-Simpson & Spiller)	Dilute, no action; concentrated, fibre blue.	Fibre at first black, which soon changes to green.	Solution pink	As with NaOH	Little action, fibre slightly blue.	Colour extracted, solution fluorescent	To detect Magdala's red on silk dyed eosin, extract with boiling alcohol, which dissolves out the eosin, and test the solution in the ordinary way. Wash the silk and test for Magdala red with acids and alkalis.
Magdala's red.	No change	No change	No change	No change	Wool brownish-red, cotton not changed.	No action	Nitric acid colours fibre bright yellow.
Madder.	Fibre brownish-red.	Fibre brownish-red, solution red.	Fibre and solution purple.	As with NaOH	As with NaOH	No action	Nitric acid colours fibre yellow.
Coeruleine	Fibre orange-red, solution orange-pink.	Fibre and solution bright pink.	Solution purple	As with NaOH	Fibre and solution orange-red.	No action	Nitric acid colours fibre brownish-yellow. Boiling soap solution removes much colour, solution bluish-red.
Peachwood	Fibre dark red, solution pink.	Fibre brown, solution yellow changing to brown.	Much colour extracted, bluish-red. Cotton almost decolourised.	As with NaOH	Fibre and solution bluish-red on heating.	Pale yellow solution.	Nitric acid colours wool dark olive.
Barwood	No action	Fibre reddish-brown, solution dirty brown.	Fibre purplish, solution colourless.	As with NaOH	Fibre unchanged, solution red.	Red solution	Nitric acid colours wool dark olive.
Sanderswood.	No action	Fibre and solution reddish-brown.	Fibre purplish, solution colourless.	As with NaOH	Fibre unchanged, solution red.	Red solution	Nitric acid colours wool dark olive. Boiled with FeSO <sub>4</sub> colour becomes violet.
Safflower	Cotton decolourised.	Cotton decolourised.	With dilute NaOH, cotton pale yellow.	Cotton flesh-coloured.	Cotton straw yellow.	No action	—
Orchil	Solution red	Fibre and solution purple, afterwards brown.	Fibre bluish-purple.	As with NaOH	At once decolourised.	Bluish-red solution.	See Magenta.

## YELLOW AND ORANGE COLOURS.

Pteric acid	Colour extracted on boiling, liquid greenish-yellow.	Decolourised	Fibre becomes orange, solution yellow.	Fibre becomes paler, a yellow colour extracted on boiling.	Fibre bleached, the liquid colourless.	Yellow colour extracted.	All pteric acid yellows taste bitter. Heated with KCN solution fibre becomes red through the formation of isourpicric acid. In compound colours the cloth should be extracted with alcohol, and the solution tested for pteric acid with KCN.
Victoria yellow	Decolourised, washing restores the colour.	—	—	—	—	—	Warm water extracts the colour.
Naphthol yellow	Decolourised almost completely.	As with HCl	Fibre orange, solution yellow.	Fibre paler, yellow colour extracted on boiling.	Fibre bleached, the liquid colourless.	Yellow colour extracted.	Water extracts the colour and the yellow solution is decolourised by H <sub>2</sub> SO <sub>4</sub> . KCN extracts a red colour. Wrapped in white paper and heated to 120°C., leaves a stain on paper.

## YELLOW AND ORANGE COLOURS—continued.

Colouring matter	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH	NH <sub>4</sub> OH	SnCl <sub>4</sub> + HCl	Alcohol	Other tests
Naphthol yellow (S. B. A. & S. F.)	Fibre bleached, solution colourless.	Decolourised	Fibre paler, liquid yellow.	Fibre changed, liquid pale yellow.	Bleached	No action	Boiling water extracts nothing. Heated to 120°C. in white paper, leaves no stain.
Citronine (Gerber & Uhlmann)	Fibre dark red-violet. On dilution the red-violet liquid becomes magenta red.	Fibre dark violet, liquid violet.	Fibre dirty greenish yellow, solution colourless. Becomes yellow on dilution.	Fibre uncoloured, liquid colourless.	Fibre at first yellowish-brown, on heating decolourised; liquid pale yellow.	Slightly extracted.	HNO <sub>3</sub> : At first red-violet spot, becoming magenta-red in middle, and violet at the border.
Aurantia	Fibre pale yellow	Fibre yellowish drab	Little or no effect.	No action	Fibre brown on heating.	Colour readily extracted.	Heated with SnCl <sub>4</sub> gives dark brownish-red colour, afterwards decolourised.
Fast yellow (B. A. & S. F.)	Red	Fibre brownish-red, liquid red.	Solution brownish-yellow.	Little action	Fibre brightened, afterwards decolourised.	A little colour extracted.	HNO <sub>3</sub> gives a bright-red spot.
Crocin orange (Fr. Bayer & Co.)	Fibre reddish-brown, liquid pink.	Fibre darker, liquid orange. On washing the fibre becomes orange again.	Fibre orange-brown, liquid very slightly coloured.	No action	Almost no action in the cold; on boiling quickly and completely decolourised.	No action, or only very slight orange-red colour.	HNO <sub>3</sub> : Blue-black spot. Bleaching powder: Fibre brownish, then decolourised.
Chrysoidine (Brook, Simpson & Spiller)	Fibre red	Yellow colour extracted	Fibre paler and yellower.	Fibre yellower	Almost decolourised.	Yellow colour extracted.	—
Orange 3 (Fr. Bayer & Co.)	Fibre red, liquid pink	Fibre and liquid bright bluish-red.	Fibre dull yellowish red.	Fibre not changed, liquid slightly yellow.	Completely bleached.	A little colour extracted.	—
Orange 4 (A. Poirrier)	Fibre reddish-violet, liquid violet.	As with HCl	No action	Fibre not changed, liquid yellow.	At first fibre becomes deep violet, on heating gradually lighter and finally bleached.	Yellow colour extracted.	—
Orange 2 (A. Poirrier)	Fibre and liquid bluish-red.	As with HCl, but bluer	Fibre deep red	No action	Completely bleached.	No action	—
Ortol. (J. R. Geigy & Co.)	Dil. HCl: No action. Conc. HCl: Fibre dark red, liquid bright red. On dilution again yellow.	As with HCl	Fibre orange-red, liquid colourless.	Fibre orange-yellow, liquid scarcely coloured	Fibre at first light yellow, then gradually decolourised; liquid colourless.	No action	HNO <sub>3</sub> : No action. HNO <sub>3</sub> : pale orange-red spot. The colouring matter is disengaged by its remarkable fastness to light.
Primuline yellow (Brook, Simpson & Spiller)	No action	Fibre at first brighter and darker yellow, then pale yellow.	Fibre brighter and orange-yellow; liquid colourless.	No action	Slight action	No action	HNO <sub>3</sub> : The fibre becomes rather dark orange; treated with NH <sub>4</sub> fume orange-brown, with Betanaphthol red.
Primuline orange (Brook, Simpson & Spiller)	Fibre red-brown, liquid also red-brown.	Fibre orange-brown, liquid dark red.	Fibre dark red-brown, liquid slightly coloured. As with brilliant yellow.	No action	Fibre at first orange-brown, then decolourised.	Colour somewhat extracted.	HNO <sub>3</sub> : Red-brown spot.
Curcumin W. (Berlin Aniline Co. Leobardt & Co.)	Dil. HCl: No action. Conc. HCl: Fibre violet black, liquid slightly coloured.	Fibre violet-black, liquid beautiful violet. On dilution blue.	Fibre dark red-brown, liquid slightly coloured. As with brilliant yellow.	As with brilliant yellow.	Fibre at first brownish-yellow, then decolourised.	No action	—
Chrysamine (Fr. Bayer & Co.)	Dil. HCl: Fibre pale yellow, red-brown on dilution becomes yellow. Conc. HCl: Conc. HCl: Fibre bright pink on dilution.	Fibre magenta-red, liquid red-violet.	Fibre dark orange, liquid scarcely coloured.	Fibre bright orange, liquid colourless.	Fibre at first dirty yellow, gradually decolourised.	No action	HNO <sub>3</sub> : Brown spot gradually becoming reddish grey.
Brilliant yellow (Leobardt & Co. Fr. Bayer & Co.)	Dil. HCl: No action. Conc. HCl: Fibre dark violet, liquid slightly coloured.	Fibre violet-black, liquid violet.	Fibre cherry-red, liquid slightly pink.	As with NaOH	Fibre at first dirty yellow, then quickly and completely decolourised.	No action	—
Hessian yellow (Leobardt & Co. Fr. Bayer & Co.)	Dil. HCl: Fibre brighter. Conc. HCl: Fibre black, liquid violet.	Fibre dark violet, liquid red-violet.	Fibre beautiful dark-red, liquid bright pink.	Fibre dark orange, liquid slightly orange-red.	Fibre at first pale yellow, gradually completely decolourised.	No action	HNO <sub>3</sub> : Brownish spot with bright yellow border. HNO <sub>3</sub> : Acts like dilute HCl.

Chrysophanone (Fr. Bayer & Co.)	Dil. HCl : No action. Conc. HCl : Fibre violet- black, liquid scarcely coloured.	Fibre brown, then dark red-violet. On dilution blue.	Fibre unchanged, liquid slightly yellowish.	No action	Fibre at first brownish yellow, then deco- lourised.	HNO <sub>3</sub> : No action. HNO <sub>3</sub> : Violet spot.
Toluylene orange (K. Oehler & Co.)	Dil. HCl : Fibre more pink. Conc. HCl : Fibre paler, liquid yellow. On dilution the solution be- comes flesh colour, the fibre pink.	Fibre yellowish, liquid yellow.	Fibre more orange-red, li- quid colourless.	No action	Fibre at first pink, becomes decolourised on boiling rather slowly.	HNO <sub>3</sub> : The fibre becomes greyish- black, treated with NH <sub>3</sub> changes to reddish-grey. HNO <sub>3</sub> : Dirty reddish- violet spot, gradually becoming grey.
Toluylene orange (G. Oehler & Co.)	Dil. HCl : No action. Conc. HCl : Fibre violet, liquid reddish. On dilu- tion the fibre and liquid regain original colour.	Fibre magenta-red, liquid not strongly coloured.	Fibre bright orange-red, li- quid slightly co- loured.	No action	Fibre at first more pink, on boiling decolourised; liquid colourless.	HNO <sub>3</sub> : Fibre becomes grey; which if treated with NH <sub>3</sub> turns dirty yellow.
Tartrazine (B. A. & S. F.)	Fibre more orange, liquid yellow.	As HCl	Fibre more orange, liquid orange- yellow.	As NaOH, only actionless marked.	Upon heating de- colourised.	HNO <sub>3</sub> : No action.
Auramine (B. A. & S. F.)	Fibre almost decolourised, liquid colourless. On di- lution the yellow colour is partly restored.	Fibre decolourised, liquid colourless.	Fibre decolourised, liquid colourless. On washing the yellow colour is partly restored.	Fibre paler, liquid colourless.	Gradually decolourised in the cold, on heat- ing very rapidly.	HNO <sub>3</sub> gives a white spot, which gradually turns orange in the middle, leaving a white border. Compare quinoline yellow.
Quinoline yellow (B. A. & S. F.)	Fibre yellow, liquid colour- less. On diluting, the original pale-yellow colour is restored.	As with HCl	Fibre at first deeper yellow, then gradually decolourised. The yellow colour is restored on wash- ing.	Almost without action.	In the cold no action. On heating, fibre becomes somewhat paler.	HNO <sub>3</sub> gives a deep yellow spot pro- bably only due to the action of the HNO <sub>3</sub> upon the wool.
Nitro-alizarin	Fibre pale straw-yellow, solution yellow.	Fibre brownish-yellow, liquid yellow.	Fibre claret red or brownish, liquid colourless.	Cold, no action; hot, as with NaOH, but fibre not so dark.	Fibre deep yellow, liquid yellow.	HNO <sub>3</sub> gives a bright yellow spot. Boiling dil. OH <sub>2</sub> colours the fibre claret red.
Gallofavin (B. A. & S. F.)	Fibre rather darker; liquid yellow. On dilution fibre and liquid almost colour- less.	As with HCl	Fibre rather darker and more orange-yellow, liquid yellow.	Fibre darker and slightly olive- green, liquid al- most colourless.	No particular action.	Warned with Fe <sub>2</sub> Cl <sub>6</sub> fibre becomes dirty olive-green.
Phosphine	Fibre nearly decolourised, solution yellow.	Solution greenish-yellow.	Fibre becomes paler and yel- lower.	Fibre becomes paler, a bright yellow.	Fibre nearly decolour- ised.	—
Anthracin (J. R. Geigy & Co.) (Obtained from a natural yellow colouring mat- ter.)	Fibre rather greenish- yellow, liquid the same. On addition of water fibre and liquid become colourless.	As with HCl	Fibre rather deeper yellow, liquid slightly yellow.	Fibre unchanged, liquid very slightly yellow.	Fibre rather brighter, liquid the same. On boiling no further decolourisation takes place.	HNO <sub>3</sub> : Brown spot, which gradually becomes pale brown in the middle, and remains dark at the border. Fe <sub>2</sub> Cl <sub>6</sub> : Fibre and liquid olive-green. Alum does not give the characteris- tic fluorescence of fustic. The ash contains chromium or aluminium. Anthracin and xanthopuric might both be derived from Persian berries. These reactions show that both colouring matters, if not identical, are at any rate very nearly allied. The dyed samples tested were mor- danted with aluminium acetate Heated with Fe <sub>2</sub> Cl <sub>6</sub> fibre becomes olive-brown.
Xanthaurin (J. R. Geigy & Co.) (Obtained from a natural yellow colouring mat- ter.)	Like anthracin.	Like anthracin.	Like anthracin.	Like anthracin.	Like anthracin.	
Madder	Little action	Fibre brownish-red, solu- tion red.	Fibre and solution purple.	Fibre brown	Fibre unchanged, so- lution pale red.	



## RED COLOURS—continued.

Colouring matter	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH	NH <sub>4</sub> OH	SnCl <sub>3</sub> + HCl	Alcohol	Other tests
Old fustic	Fibre and solution orange.	Fibre and solution brown.	Fibre changed.	Fibre unchanged, solution yellow.	Fibre orange, solution colourless.	No action	With HNO <sub>3</sub> , fibre pale yellow. Heated with FeCl <sub>3</sub> , fibre becomes olive. Boiled with acetate of aluminium gives yellow solution with bluish-green fluorescence.
Young fustic	Fibre unchanged, solution pale yellow.	Fibre and solution reddish-brown.	Fibre reddish-brown.	As with NaOH	No action	No action	With HNO <sub>3</sub> , fibre dark brown. Heated with FeCl <sub>3</sub> , fibre becomes olive.
Weld	Fibre little affected, solution pale yellow.	Fibre brownish-yellow	Fibre little affected, solution pale yellow.	No action	Fibre little affected.	No action	With HNO <sub>3</sub> , no action. Heated with FeCl <sub>3</sub> , fibre becomes olive. Colour unchanged by boiling with lead acetate.
Quercitron bark	Fibre little affected, solution yellow.	Fibre brownish-yellow, solution yellow.	Fibre changed, solution yellow.	Fibre unchanged, solution yellow.	Fibre little affected, solution yellow.	No action	With HNO <sub>3</sub> , fibre light brown. Heated with FeCl <sub>3</sub> , fibre becomes olive. Colour becomes orange by boiling with lead acetate.
Flavio	Fibre and solution yellow.	Fibre and solution yellow.	Fibre and solution yellow.	Fibre little affected, solution yellow.	Fibre brownish-yellow, solution bright yellow.	No action	With HNO <sub>3</sub> , fibre dark brown. Heated with FeCl <sub>3</sub> , fibre becomes olive. Boiling acetic acid gives yellow solution with green fluorescence. Colour becomes orange by boiling with lead acetate.
Persian berries	Fibre unchanged, solution yellow.	Fibre orange-brown, solution greenish-yellow.	Fibre unchanged, solution brownish-yellow.	Colour slightly extracted.	Fibre brown, solution yellow.	No action	With HNO <sub>3</sub> , fibre brown. Heated with FeCl <sub>3</sub> , fibre becomes olive. Colour becomes orange by boiling with lead acetate.
Turmeric	Fibre reddish-brown, solution colourless.	Fibre reddish-brown, solution brown.	Fibre bright reddish-brown, solution orange-brown.	Fibre bright reddish-brown, solution orange.	Fibre reddish-brown, solution colourless.	Colour extracted, solution orange or yellow with green fluorescence.	With HNO <sub>3</sub> , fibre pale yellow. Boracic acid added to HCl and alcoholic solution gives bright red colour.
Annatto (on cotton), Iron-buff (on cotton), Chrome yellow (on cotton),	Little affected, or brownish red.	Fibre and solution blue	Little affected	As with NaOH	Decolourised	Solution bright yellow.	Dyed blue with K <sub>2</sub> FeC <sub>2</sub> O <sub>8</sub> + HCl.
	Fibre straw-yellow or decolourised.	Little action	No action	No action	Decolourised	No action	Fibre blackened with ammonium sulphide or H <sub>2</sub> S.
	Fibre decolourised, solution pale yellow.	Fibre greenish-yellow or dull yellow.	Fibre paler, liquid pale yellow.	Little action	Decolourised	No action	—

## GREEN COLOURS.

Colouring matter	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH	NH <sub>4</sub> OH	SnCl <sub>3</sub> + HCl	Alcohol	Other tests
Resorcin green (Durand & Huguenin.)	Fibre grey-yellow, liquid orange-red.	Fibre bright brown, liquid the same. On dilution no change of colour.	Fibre slightly darker, liquid greenish	No action	Slightly decolourised, liquid brownish.	No action	HNO <sub>3</sub> ; yellow-brown spot. The ash contains iron.
Malachite green	Fibre and liquid bright orange; on washing with water the green colour is restored.	Fibre much bleached, liquid bright orange	Decolourised	Decolourised	Fibre almost decolourised, liquid yellow.	Green colour extracted.	Heated to 100°C. colour does not change to bluish-grey. (Distinction from methyl green.)
Helvetia green (Soc. Chim. Ind., Basle.)	Liquid yellow; green colour restored on diluting with water.	Decolourised	Fibre buff-yellow.	As with NaOH	Almost completely decolourised.	Bluish-green colour extracted.	
Acid green (Soc. Chim. Ind., Basle.)	Fibre pale green	Fibre brown, liquid yellow	Decolourised	Decolourised	Fibre almost decolourised, liquid yellow.	Green colour readily extracted.	
Alkali green	Fibre dark olive-green, solution reddish-brown.	Fibre and solution dark brown.	Decolourised	Decolourised	Fibre not changed, bluish-green colour extracted	Green colour extracted.	

Methyl green (B. A. & S. F.)	Fibre and liquid pale yellow; colour restored on washing.	Fibre much bleached, liquid colourless.	Decolourised	Decolourised	Fibre almost decolourised, liquid yellow.	Bluish-green colour extracted.	Heated to 100°C. becomes bluish-violet. (Distinction from Malachite green.)
Aldehyde green	Fibre bright yellow	Fibre orange	Little action, fibre afterwards paler	At first little action, afterwards bleached.	Slowly decolourised	Green colour extracted.	HNO <sub>3</sub> gives a brown spot.
Cerulein (B. A. & S. F.)	Fibre duller green, liquid claret-red.	As with HCl, liquid dirty amber yellow.	No action	No action	Fibre brownish-red, liquid brown; on washing with water, colour gradually restored.	No action	HNO <sub>3</sub> gives a brown spot.
Vat-indigo and old fustic.	Fibre paler, liquid blue	As with HCl	Fibre greenish-blue, liquid yellow	Fibre paler blue, liquid yellow or greenish	Fibre much paler, liquid greenish-yellow.	See Indigo	Boiling glacial acetic acid gives green solution; on diluting with water blue is precipitated. Boiling Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> gives yellow solution with green fluorescence. Remove yellow colour by boiling with dilute Na <sub>2</sub> CO <sub>3</sub> , and test the blue remaining for indigo. Ash contains lead. Blackened by (NH <sub>4</sub> ) <sub>2</sub> S. Bleaching-powder solution changes colour to yellow. Cold water extracts picric acid, test solution with KCN.
Vat-indigo and chromate of lead (on cotton).	Yellow removed at once, blue afterwards; liquid dull yellow.	Fibre dirty yellowish-green	Yellow removed; liquid pale yellow.	No action	Fibre becomes at first blue, afterwards decolourised	See Indigo	
Indigo - carmine and picric acid	Fibre at first blue, afterwards very pale; liquid blue.	As with HCl	Fibre almost decolourised, liquid pale yellow.	As with NaOH	Decolourised		
Chrome green (on cotton).	No action	No action	No action	No action	No action	No action	Boiled with a solution of bleaching-powder gives yellow liquid containing chromate. Occurs only on calico prints.

## BLUE COLOURS.

Azo-blue (Fr. Bayer & Co.)	Dil. HCl: No action. Conc. HCl: Fibre blue-black, liquid colourless.	Fibre blue-black, liquid blue.	Fibre cherry-red, liquid pale pink.	Fibre dark violet, red, liquid violet.	Fibre at first blue-black, then gradually decolourised.	No action	Picric acid: Fibre blackish-brown.
Benzo-azurine G (Fr. Bayer & Co.)	Fibre blue-black, liquid colourless.	Fibre blue-black, liquid more reddish-blue.	Fibre dark carmine red, liquid pale pink.	Fibre dark violet, liquid slightly cherry-red.	Decolourised only gradually.	No action	By boiling with soap solution the liquid becomes deeply coloured blue.
Victoria blue. (B. A. & S. F.)	Fibre at first blue-black, liquid reddish. On dilution the fibre becomes first green, then blue again.	As with HCl	Fibre dark brownish-red, liquid colourless.	Fibre blue-black, liquid colourless.	In the cold fibre dark blue, on boiling greenish-blue. Liquid when hot greenish, upon cooling bright blue.	Some colour extracted in the cold; on boiling much colour extracted.	HNO <sub>3</sub> : At first black spot which gradually becomes reddish-brown, and is changed by NH <sub>3</sub> to brownish-yellow, which colour remains after washing.
Spirit blue (A. Poirrier.)	Fibre dark green, solution brownish.	Fibre and solution reddish-brown.	Fibre brick-red.	Decolourised slowly.	Fibre not changed, liquid colourless.	Alcohol extracts the colour even in the cold.	HNO <sub>3</sub> gives a black spot, which changes to dark green.
Alkali blue 3 B. (B. A. & S. F.)	Fibre greenish-blue, solution almost colourless.	Fibre and liquid reddish-brown on standing.	Fibre at first reddish-brown, afterwards decolourised.	Decolourised rapidly.	Fibre not changed, liquid colourless.	Alcohol extracts the colour even in the cold.	HNO <sub>3</sub> gives a pale-green spot with black border.
Soluble blue (Brook, Simpson, & Spiller.)	Extracts blue colour.	Fibre and liquid reddish-brown.	Fibre reddish-brown.	Decolourised at once.	Fibre little changed, blue colour extracted.	Alcohol, action on boiling, extracts no colour.	HNO <sub>3</sub> gives a dark spot, which changes to dark green with a black border.
Naphthylene blue G. (Fr. Bayer & Co.)	Fibre brownish-violet; liquid brownish-orange.	Fibre brown-black; liquid dark brown. On dilution dirty blue.	Fibre brown; liquid brownish-orange.	Fibre brownish-violet; liquid bright reddish-brown.	Fibre decolourised; liquid colourless.	Liquid very slightly violet.	HCl gas is sufficient to change the blue colour of the fibre to chocolate-brown.

## BLUE COLOURS—continued.

Colouring matter	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH	NH <sub>4</sub> OH	SnCl <sub>2</sub> + HCl	Alcohol	Other tests
Alizarin blue (B. A. & S. F.)	Fibre violet, liquid yellowish-red.	Dilute H <sub>2</sub> SO <sub>4</sub> : fibre violet, liquid pale red. Concentrated H <sub>2</sub> SO <sub>4</sub> gives violet liquid.	Fibre green.	No action.	Fibre at first violet, on heating brownish-red, liquid is brown.	No action.	HNO <sub>3</sub> gives a bright yellow spot which goes brown after a time. Soap and bleaching powder have no action. Phosphoric acid gives orange-red solution, which on diluting with water and adding NH <sub>4</sub> OH becomes blue. A dilute ammoniacal alcohol solution shows characteristic absorption bands when examined with spectroscopy. Boiled with olive oil, purplish colour is extracted.
Indophenol blue	Fibre greyish-brown.	Fibre greyish-brown.	No action.	No action.	Decolourised.	Blue colour extracted.	—
New blue (Cassella & Co.)	Fibre reddish-blue.	Fibre dark grey, liquid grey.	Fibre brownish-violet, liquid slightly pink.	As with NaOH.	Fibre at first green, then almost decolourised; liquid colourless, becomes greenish again in the air, then blue.	Liquid very slightly blue.	—
Nile blue (B. A. & S. F.)	Fibre at first greenish, then orange-yellow; liquid orange-yellow.	Fibre and liquid brown-red. On dilution at first yellow, then green, finally blue again.	Fibre red, liquid pink.	Fibre violet.	Fibre at first green, then decolourised; liquid colourless, becomes greenish-blue in the air.	Liquid very slightly blue.	HNO <sub>3</sub> : Yellow spot, becoming green in middle and yellow at the border.
Methylene blue (B. A. & S. F.)	Fibre nearly decolourised, solution bluish-green.	Fibre and liquid green.	Fibre bluish-violet.	No action.	Decolourised.	Greenish-blue colour extracted.	HNO <sub>3</sub> gives a green spot which does not change further. Bleaching-powder solution turns it first green, and gradually decolourises it. On cotton it is much faster than aniline blue, and withstands neutral soaps, light, and weak bleaching-powder. Very sensitive to chromic acid. A 3 p.c. solution of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> changes it first to violet and finally decolourises it. If it has been fixed with tannin a brown colour is left.
Basic blue (Durrand & Huguenin.)	Fibre dark grey, liquid yellow. Upon dilution the fibre becomes blue again.	Fibre at first blue-black, then green, and finally yellowish; liquid yellow. On dilution both become blue again.	Fibre darker.	No action.	No action.	Liquid very slightly blue.	—
Induline	Fibre violet, liquid deep blue.	Solution dark blue.	Reddish-violet colour abstracted, the solution decolourised on addition of zinc powder, restored colour on exposing film to red solution to the air.	As with NaOH.	Extracts a violet or green colour.	Bluish-violet colour extracted.	Induline NN is not changed by bleaching-powder solution. HNO <sub>3</sub> gives a dark bluish-green spot. Bleaching-powder solution changes some indulines to a reddish-grey, whilst others are decolourised.
Resorcin blue	—	Dilute H <sub>2</sub> SO <sub>4</sub> , no action.	Solution blue, with red fluorescence.	As with NaOH.	—	—	—



Dye	Colour	No action	Dilute $H_2SO_4$ no action. Conc. $H_2SO_4$ gives a blue solution.	No action.	On heating fibre becomes paler, so solution greenish-yellow.	Boiling absolute alcohol gives bright yellow spot. Indigo-dyed cotton if burnt gives off purple vapour which can be condensed on a cold porcelain slab as a blue spot.	Chloroform extracts blue colour. Strong $HNO_3$ gives bright yellow spot.
Indigo carmine.	Solution greenish-blue.	No action.	Solution blue.	Fibre greenish. On boiling with dilute NaOH colour abstracted, solution little coloured, but becomes blue on acidifying.	Fibre decolourised on heating.	Little or no colour extracted.	Colour extracted by boiling with dilute $Na_2CO_3$ ; silk or wool may be dyed in the acidified solution. Nitric acid gives yellow spot.
Prussian blue	No action.	No action.	No action.	Fibre brown on heating.	No action.	No action.	Ash contains iron. Concentrated nitric acid gives green spot. Boiled with NaOH, solution contains potassium ferricyanide, on acidifying and adding $FeCl_3$ blue precipitate is obtained. If used for toning vat-indigo blue, it can be removed by boiling with dilute HCl, the indigo being unaffected thereby. blue-coloured ash remains. Only used with on calico or woollen prints.
Logwood blue	Fibre red or brown, solution red.	No action.	As with HCl	Fibre and solution purple.	As with NaOH	No action.	No action.
Ultramarine blue.	Decolourised	No action.	Decolourised	No action.	No action.	No action.	No action.

## VIOLET COLOURS.

Dye	Colour	No action	Dilute $H_2SO_4$ no action. Conc. $H_2SO_4$ gives a blue solution.	No action.	On heating fibre becomes paler, so solution greenish-yellow.	Boiling absolute alcohol gives bright yellow spot. Indigo-dyed cotton if burnt gives off purple vapour which can be condensed on a cold porcelain slab as a blue spot.	Chloroform extracts blue colour. Strong $HNO_3$ gives bright yellow spot.
Azo-violet (Fr. Bayer & Co.)	Dil. HCl : Fibre blue. Conc. HCl : Fibre blue-black ; liquid blue-green.	No action.	Fibre blue-black ; liquid blue-green.	Fibre carmine-red ; liquid magenta-red.	Decolourised slowly.	No action.	Picric acid : Fibre black. Dilute acetic acid changes the violet colour to blue.
Heliotrope	Dil. HCl : Fibre dark blue-black ; liquid blue.	No action.	Fibre blue-black ; liquid blue.	No particular action.	Fibre at first dark grey ; then decolourised.	No action.	$HNO_3$ : Fibre becomes greenish-grey ; on washing and treating with $NH_4OH$ is changed to brownish-orange ; liquid slightly brownish. Picric acid : Fibre dark brown.
Hessian violet (Fr. Bayer & Co. Leonhardt & Co.)	Fibre dark blue ; liquid scarcely coloured.	No action.	Fibre dark blue ; liquid blue.	Fibre redder ; liquid slightly reddish-violet.	Fibre at first beautiful blue ; decolourised by continued boiling.	No action.	$HNO_3$ : Fibre becomes dirty grey-violet, changed to dirty carmine-red by NaOH. $HNO_3$ : Orange spot with blue border.
Methyl violet	Fibre yellowish-brown, liquid amber-yellow ; the violet colour restored on diluting with water.	No action.	As with HCl	Fibre pale lilac, nearly decolourised.	Fibre green but nearly decolourised on standing, liquid yellowish-green.	Colour extracted.	
Benzyl violet	Fibre yellowish-brown, liquid amber-yellow ; the violet colour restored on diluting with water.	No action.	As with HCl	Almost decolourised, fibre pale bluish-lavender.	Fibre pale green, liquid pale yellow.	Colour extracted.	
Phenyl violet or Spirit violet. Acid violet 7B (Fr. Bayer & Co.)	Fibre dark green, solution brownish.	No action.	Fibre and solution reddish-brown.	Decolourised	Blue colour extracted ; only decolourises slowly.	Colour extracted.	$HNO_3$ gives a green spot.
	Fibre green, liquid reddish-brown ; on dilution green-blue.	No action.	Fibre at first blackish, then brown, then brownish-red ; liquid brownish-red on dilution green-blue.	As NaOH	Fibre beautiful green ; liquid blue-green. On dilution fibre and liquid both blue.	Liquid scarcely coloured violet.	$HNO_3$ : No action. $HNO_3$ : First olive-green, then dirty yellow spot. On washing remains unchanged.

## VIOLET COLOURS—continued.

Colouring matter	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH	NH <sub>4</sub> OH	SnCl <sub>4</sub> +HCl	Alcohol	Other tests
Fast violet (Fr. Bayer & Co.)	Fibre dark blue-black; liquid slightly bluish.	Fibre black; liquid grey-blue. On dilution solution at first, green-blue, then red; fibre again violet.	Fibre blue-black; liquid slightly violet.	Fibre unchanged; liquid slightly violet.	Decolourised gradually in the cold; rapidly on boiling.	Very slightly colourised violet.	HNO <sub>3</sub> : Blue-black spot.
Naphthylamine violet (on cotton), Gallot.	Fibre grey.	As with HCl.	Little or no action. Colour of fibre bluer.	No action.	Fibre crimson, liquid red.	No action.	HNO <sub>3</sub> gives a bright yellow spot. Bleaching-powder solution has no action.
Alizarin	Fibre and liquid dull yellow.	As with HCl.	Colour of fibre bluer.	No action.	As with HCl.	No action.	Destroy the colour by boiling with dilute HCl, wash and add NaOH; the alizarin remaining on the fibre is dissolved with purple colour.
Galloyaniline (Dürand and Huguenin.)	Fibre violet; liquid beautiful violet.	Fibre dark blue-black, liquid intense Prussian blue; on dilution bright magenta-red.	Fibre violet-black; liquid purple-violet.	As NaOH, only rather slight action.	Fibre in the cold becomes yellowish-green; liquid colourless.	No action.	HNO <sub>3</sub> : Fibre dirty grey-violet; liquid at first blue-green, then green, and finally yellow.
Miscorine (Dürand and Huguenin.)	Fibre blue-black; liquid dirty blue.	Fibre greenish black, liquid greenish; on dilution dirty violet.	Fibre brownish black; liquid scarcely colourised.	Fibre violet-blue; liquid scarcely violet.	Fibre blackish; on heating blue, then greenish and finally yellowish-grey.	No action.	HNO <sub>3</sub> : Black spot.
Perkin's violet	Fibre unchanged, solution bluish-pink.	Little or no action.	Fibre blue, colour restored on washing.	No action.	Fibre dirty brown, but not decolourised.	Colour extracted.	HNO <sub>3</sub> has no effect. Cl bleaches the colour slowly.

## BLACK COLOURS.

Colouring matter	HCl	H <sub>2</sub> SO <sub>4</sub>	NaOH	NH <sub>4</sub> OH	SnCl <sub>4</sub> +HCl	Alcohol	Other tests
Wool black (Berlin Aniline Co.)	Fibre remains black; liquid pale blue; on dilution pink.	As with HCl.	In the cold no action, on boiling fibre dark violet; liquid violet.	No action.	Fibre decolourised.	No action.	HNO <sub>3</sub> : after some moments, bright red-brown spot.
Naphthol black (M. L. & Br.)	Fibre remains black, liquid reddish.	Fibre remains black, liquid olive-green.	Fibre remains black, liquid very slightly reddish.	No action.	On boiling, fibre becomes green; on washing it becomes blue.	No action.	HNO <sub>3</sub> : After some time a brown spot.
Brilliant black (B. A. & S. F.)	Fibre remains black, liquid slightly red-violet.	—	Fibre appears rather greener black, liquid violet-black.	Fibre remains black, liquid violet-black.	On boiling the liquid becomes dark green, finally almost decolourised; liquid colourless.	No action.	HNO <sub>3</sub> : Dark red-brown spot.
Resorcin black (Dürand and Huguenin.)	Fibre yellow-green, liquid orange-brown.	Fibre brown, liquid brown	Fibre unchanged, liquid slightly greenish.	No action.	Fibre pale brown, liquid pale brown.	No action.	HNO <sub>3</sub> : Brown-yellow spot. The ash contains iron.
Aniline black (on cotton).	No action, or colour becomes greenish-black, restored by alkalis. Acid solution brownish.	As with HCl.	No action.	No action.	Fibre greenish-grey, colour restored by NH <sub>3</sub> .	Boiling alcohol extracts a brownish-red colour.	Bleaching-powder solution changes colour to brownish-red. Several pressures through a concentrated solution of KMnO <sub>4</sub> and oxalic acid ultimately decolourise it.
Cachou de Laval (on cotton), (A. Poirrier.)	Fibre little changed, liquid slightly grey.	Fibre rather yellower, on washing original colour restored.	No action.	No action.	Fibre slightly redder or brownier.	No action.	Weak oxidising agents have no action. It seldom happens that cloth or yarn is dyed with cachou de Laval alone. As a ground colour, in most cases it is difficult to detect, but if touched with auramine, fustic, or magenta, it is not so difficult.

Alizarin black (Alizarin with iron mordant.)	Fibre orange, colour retained with $\text{NH}_3$ .	As with HCl . . .	No action . . .	No action . . .	As with HCl . . .	No action . . .	Ash contains iron. Occurs only on printed calico.
Alizarin black (B. A. & S. F.)	Fibre remains black, liquid very slight red-violet.	Fibre remains black, liquid slightly green-blue.	Fibre black, liquid pale blue.	No action . . .	On boiling the fibre becomes brownish, liquid yellow.	No action . . .	$\text{HNO}_3$ : After standing some minutes gives a dark olive-green spot.
Logwood black	Fibre red or olive-brown, solution deep red.	As with HCl . . .	Solution purple . . .	As with NaOH . . .	Fibre violet or greyish-red, solution red, afterwards brown.	No action . . .	Ash contains iron or chromium.
Woaded black	Logwood colour removed, indigo not affected, and fibre remains blue.	As with HCl . . .	Logwood colour removed, indigo not affected.	As with NaOH . . .	Fibre becomes dirty greenish-blue.	As with indigo-blue.	First remove logwood colours, &c., by boiling with dilute HCl, and test blue remaining for indigo.
Tannin black (on cotton).	Bleached to pale straw-colour, steeping afterwards in $\text{NH}_3$ gives reddish-brown colour.	As with HCl . . .	Fibre brownish-grey or black.	No action . . .	Decolourised . . .	No action . . .	Ash contains iron.

BROWN COLOURS.							
Phenyl brown	Colour extracted, solution brownish-red.	—	Purplish - brown colour extracted.	Reddish - brown colour extracted.	Fibre pink, solution colourless.	Dark brownish-red colour extracted.	—
Bismarck brown	Fibre reddish-brown, solution red.	As with HCl, but darker . . .	Fibre brownish-yellow, solution colourless.	Fibre unchanged.	Fibre almost decolourised.	Red or pink colour extracted.	Boiling water extracts colour; boiling glacial acetic acid still more, with yellowish-green fluorescence.
Fast brown BG (Berlin Aniline Co.)	Fibre dark red, violet, liquid violet. On dilution the fibre becomes brown again.	As with HCl . . .	Fibre bright dark red.	As NaOH . . .	Fibre at first darker, on boiling rapidly decolourised.	No action . . .	$\text{HNO}_3$ : Black spot, which rapidly becomes bright red-brown.
Benzobrown (Fr. Bayer & Co.)	Dil. HCl: Fibre a reddish-brown. Conc. HCl: Fibre much darker, liquid purple-red.	Fibre brown-black, liquid dark brown.	No action . . .	No action . . .	Fibre yellow and paler, liquid brownish-yellow.	Only a slight trace of colour extracted.	Benzo-brown; stands light very badly.
Naphthylamine brown.	Fibre brownish-yellow, solution orange.	—	—	Fibre yellow	Fibre purple, solution pale pink.	Solution bluish-pink.	—
Alizarin brown (with chrome mordant.)	Fibre brownish - orange, colour restored by $\text{NH}_3$ .	As with HCl . . .	Action slight, fibre bluer, liquid tinted blue.	Fibre unchanged . . .	As with HCl . . .	No action . . .	—
Andraecine brown (B. A. & S. F.)	Fibre paler and redder, liquid chestnut-brown; on dilution yellow.	Fibre paler and redder, liquid chestnut-brown; on dilution yellow.	Fibre black, liquid grey.	Fibre brownish-grey, liquid scarcely coloured.	Fibre brownish yellow, liquid the same.	Only a slight trace of colour extracted.	$\text{HNO}_3$ : Black spot.
Nitroalizarin (with chrome mordant.)	Fibre paler, liquid yellow.	Fibre darker, liquid orange	Fibre darker, solution colourless.	No action . . .	As with HCl . . .	No action . . .	—
Catechu brown	Little or no change, solution pale orange.	Little or no change . . .	Little or no change	Little or no change	Fibre becomes paler, solution colourless or orange.	No action . . .	Ash contains chromium and sometimes copper. Colour more or less bleached by boiling solution of bleaching-powder. Occurs only on wool.
Camwood brown (with chromium mordant.)	Fibre red, liquid yellowish-red.	As with HCl . . .	Fibre and liquid purple.	Fibre purple, liquid colourless.	Fibre and liquid cherry-red.	—	—
Peachwood brown (with chromium mordant.)	Fibre and liquid yellowish-red.	Fibre yellowish-red, liquid yellow.	Fibre purple, liquid cherry-red.	Fibre purple, liquid colourless.	Fibre and liquid cherry-red.	—	—
Dye-wood brown (mixture of dye-woods).	Red or purple colour extracted.	As with HCl . . .	Little change, liquid tinged red.	Fibre unchanged, liquid tinged red.	Fibre redder, solution reddish.	No action . . .	Ash contains aluminium and iron.
Manganese brown	Slowly decolourised . . .	No action . . .	No action . . .	No action . . .	Rapidly decolourised . . .	No action . . .	Ash contains manganese.



COPAIVENE *v.* OLEO-RESINS.COPAIVIC ACID *v.* OLEO-RESINS.COPAL *v.* RESINS.COPAL VARNISH *v.* VARNISH.COPELIN *v.* RESINS.COPIVI *v.* OLEO-RESINS.

**COPPER.** Symbol Cu. At. wt. = 63.1. This is undoubtedly one of the earliest known metals. Occurring in large masses in the metallic state, easily distinguishable by its colour, and possessing valuable mechanical properties, copper could not fail to attract attention. Many of its ores, too, possess brilliant colours, and one of them, malachite, was used for the purposes of ornament at a very early date.

The native copper of the Lake Superior region was worked by the pre-historic inhabitants of the North American continent, and amongst the specimens of metal-work discovered by Dr. Schliemann in his researches at the ruins of Troy, was one consisting of pure copper. At a very early period, however, the knowledge of metallurgy had made such progress that the influence of the presence of other elements on the physical properties of copper had become known.

Thus, the use of tin to harden copper, and so to render it serviceable for tools and weapons, was known in pre-historic times. The discovery of the metallurgy of copper, in so far as it relates to the reduction of copper from its ores, has been attributed to Cadmus and to Tubal Cain, but it is far more probable that it was discovered accidentally in various parts of the world, either by the lighting of fires on the outcrops of copper lodes or by such other simple means. At a very early period copper was exported from the island of Cyprus, and it is from this island that it has obtained its name. A native writer states that, previous to the seventh century A.D., Japan, though it abounds in ores of copper, obtained its supplies of that metal from China. The metallurgical processes which were then introduced, and which are still in use, do not differ essentially from those employed elsewhere.

At the present time, copper in its native state forms but a very small proportion of the source of supply of that metal. By far the larger quantity is obtained by the treatment of its compounds with other elements. The chief of these are the following:—

Name	Composition	Colour	Streak	Hardness	Density
Cuprite . . .	Cu <sub>2</sub> O	Red	Brown-red	3.5-4	5.7-6.0
Malachite . . .	CuCO <sub>3</sub> + H <sub>2</sub> CuO <sub>2</sub>	Green	Green	3.5-4	3.7-4.1
Azurite . . .	2CuCO <sub>3</sub> + H <sub>2</sub> CuO <sub>2</sub>	Blue	Blue	3.5-4	3.5-3.8
Copper pyrites . . .	Cu <sub>2</sub> S, Fe <sub>2</sub> S <sub>3</sub>	Yellow	Black	3.5-4	4.1-4.3
(Yellow copper ore)					
Bornite . . .	3Cu <sub>2</sub> S, Fe <sub>2</sub> S <sub>3</sub>	—	Black	3	4.9-5.1
(Purple copper ore)					
Fahl ore . . .	Variable	Steel-grey	Black	3-4	4.3-5.4
(Grey copper ore)					
Copper glance . . .	Cu <sub>2</sub> S	Lead-grey	Lead-grey	2.5-3	4.8-5.8

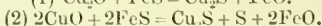
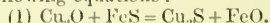
Copper also occurs in the form of the black oxide, silicates, phosphates, arseniates, sulphates, oxychloride, &c., but these minerals are not of sufficient metallurgical importance to render them ores of copper in the ordinary sense of the term. Large quantities of copper are obtained from the cupriferous iron pyrites of Spain and Portugal, which, containing as it does but 3 or 4 p.c. of copper, is yet of importance as a source of copper, owing to the small quantities of gold and silver which are also present.

Of the various ores the sulphides are by far the most important, the oxidised compounds being no longer found in any large quantities. Fahl ore is of importance, less from the point of view of the copper it contains than from that of the silver or mercury also present.

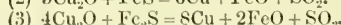
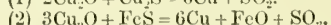
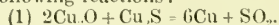
The metallurgical processes for the reduction of copper from its ores are of two main types: (1) Processes involving fusion; and (2) Wet processes not involving fusion. Each of these classes may be further subdivided. Of those processes which involve fusion, the more important are the following:—

1. *The reaction process.*—In this process, which is applied to the treatment of sulphurised ores, use is made of the greater affinity for sulphur possessed by copper than that possessed by other metals associated with it in its ores. Of these metals the most important is iron. To separate the copper, the ore is first submitted to

the action of air at an elevated temperature, and is then fused. By this means a portion of the sulphur is oxidised and passes away in the form of sulphur dioxide, care being taken to regulate the percentage of sulphur remaining in the 'calcined' ore. On fusion, the copper oxide in the ore reacts with the iron sulphide, forming cuprous sulphide and ferrous oxide, as is shown by the following equations:



The ferrous oxide so produced combines with silica, also present in the mixture treated, to form a fusible slag. When, by repeated oxidations and fusions, most of the iron, and with it the other impurities also present, have been eliminated, and the cuprous sulphide obtained comparatively free from iron, it is partially oxidised, and then, the temperature being raised, the oxides and residual sulphides react on one another, producing metallic copper by virtue of the following reactions:



2. *The reduction process.*—This process is applicable to oxidised ores, or to ores which have been oxidised by roasting, or, as it is termed in the case of the metallurgy of copper, 'calcination,' the term 'roasting' being made to apply to that stage of the reaction process in which

the metallic copper is produced. The process consists in treating, at an elevated temperature, the oxidised ore or products with carbon, usually in the form of coke or charcoal, though certain other fuels are occasionally employed. The carbon in the fuel combines with the oxygen in the ore and liberates the copper, as is shown by the following equation:  $\text{Cu}_2\text{O} + \text{C} = 2\text{Cu} + \text{CO}$ .

The reduction process is rarely used alone, but in certain important methods of treatment it is employed instead of the 'roasting' stage of the reaction process.

The metallic copper thus produced by each of these processes is not sufficiently pure to admit of its being used for industrial purposes. It contains iron and other impurities, and has first to be refined. This consists in subjecting the metal to an oxidising fusion. By this means, as most of the impurities in the copper possess a greater affinity for oxygen than does the copper itself, they are for the greater part eliminated at an early stage of the operation. Some of the copper is, however, also oxidised and passes into the slag, whilst, on the other hand, some of the impurities remain with the copper. The copper would be greatly affected by these residual impurities, were it not that the presence of a certain quantity of dissolved cuprous oxide acts to such an extent beneficially that, provided the quantities of the impurities present do not exceed certain limits, the quality of the metal is not sensibly deteriorated. In detail these processes are as follows:—

### 1. THE REACTION PROCESS.

The first stage of this process consists in the partial oxidation of the sulphur—the ore is 'calcined.' This calcination is effected in different ways, the variations adopted being dependent on the nature of the ore and of the impurities that are present. In those cases in which arsenic or antimony occurs in the ore, the calcination has to be effected with very great care in order to eliminate these impurities as completely as possible. To effect this, the ore may be heated out of free access of air so as to sublime as much as possible of the impurity in the form of sulphide, or the ore may be submitted to a careful calcination, and then fine coal or other carbonaceous materials be added to the charge in order to decompose the arseniates and antimonates produced by the oxidising action of the furnace gases. Another method consists in the addition of pyrites in order to assist in the formation and sublimation of arsenic sulphide. Yet another method consists in calcining the ore 'sweeter' than would otherwise be done, leaving, that is, less sulphur in the calcined ore. On the subsequent fusion there is then present in the charge a quantity of sulphur which is not sufficient to combine with the whole of the copper, and a reaction between the residual cuprous oxide and some of the sulphide ensues, forming metallic copper, by virtue of the reaction already given. It is found that the copper so produced is exceedingly impure, and it is possible in this way to eliminate much of the impurities, such as arsenic and antimony, which are present in the charge. Any gold and silver which may be present in the ore mixture

treated, also pass to a large extent into these copper 'bottoms,' and this, therefore, forms a means for the separation of the precious metals present in the charge.

The calcination is effected either in heaps, kilns, or reverberatory furnaces.

Heap calcination has two modifications— $\alpha$ , That in which the sulphur is not collected; and,  $\beta$ , that in which it is. This second modification is, however, comparatively unimportant.

In heap calcination, or roasting by the first method, the ground on which it is proposed to erect the heap is carefully selected and levelled, and then a bed is made of stones, slag, or other similar material, raised at least two inches above the level of the surrounding ground. This bed is then carefully faced with clay and is rolled down with heavy rollers. On the bed so prepared fine ore is strewn to the depth from 4 to 6 inches. On this is placed a layer of wood, usually in the form of logs, from 8 to 14 inches high, and the ore to be roasted is piled on top of it. Vents are left in the wood bed which communicate with central flues rising up through the ore heap. This is then covered over with finely divided ore that has already been calcined, hollows being left in covering. In these a portion of the sulphur collects that is sublimed during the burning of the heap. By opening some of these vents and closing others, the rate and manner of the combustion may be easily regulated.

The height of the ore heap depends on the richness of the ore. The higher is the heap the greater will be the temperature, and the greater will be the liability of the ore to clot. Thus ore containing 12 p.c. of sulphur may be piled to a height of some 7 feet, whilst ore containing 35 to 40 p.c. should not be piled higher than 5 or 5½ feet. The average height is about 6 feet.

The lumps of roasted ore obtained by this process frequently show a remarkable change. They have become in the centre richer in copper than they were originally, and, conversely, the outer crust is richer in iron and much poorer in copper than was that of the original lump of ore. In the case of poor ores this fact may afford the possibility of treating commercially such ores as could not otherwise be smelted. The process is known as 'kernel roasting.'

A modification of heap roasting consists in the use of 'stalls.' These, as their name implies, are usually roofless walled inclosures. They are open at the top and vary in size, but a common form is some 8 feet long, 6 feet high, and 6½ feet wide. A number of these are placed side by side and back to back. The back walls are frequently perforated, the openings leading to a central flue lying between two rows of stalls. This flue may be either connected with the stack direct, or the gases may be conducted through it to the sulphuric acid chambers. The bed slopes slightly, and in front there is a narrow fire-grate. In charging such a stall, a layer of wood is placed on the bed as in heap-roasting, and the ore piled up on it, fine roasted ore being carefully thrown over the top, and stamped down. The wood is then kindled by lighting a fire on the narrow fire-grate in front of the stall, and the further combustion may be easily regulated. Occasionally channels are left in the

side or dividing walls of the stalls, by which air may be permitted to enter to further the combustion of the sulphur and the consequent roasting of the ore. Roasting in stalls is very much more effective than roasting in heaps; the escaping sulphurous anhydride may be utilised, and the time required for the operation is greatly diminished.

Ores poor in sulphur are usually roasted in kilns. These vary considerably in form and size. In principle they resemble eupola furnaces, but as the temperature required in the kiln is comparatively low, the zone of combustion is larger, and the ratio of width to height is considerably greater in the kiln than it is in the cupola. The ore is charged in through an

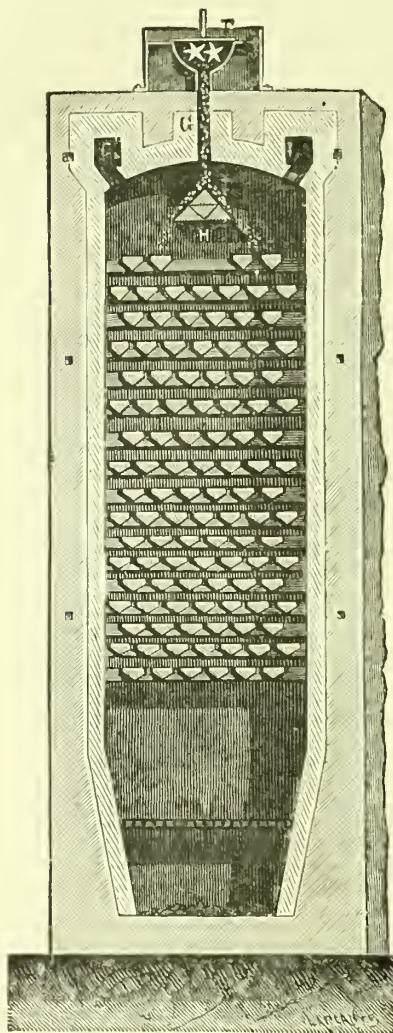


Fig. 1.

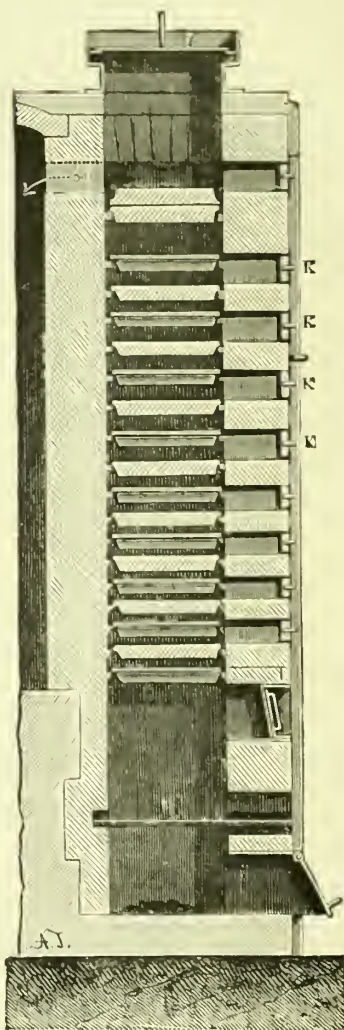


Fig. 2.

opening at the top, and air for the combustion of the sulphur is admitted through the fire-bars or other openings at the base. At the sides are several series of working doors or openings. The roasted ore is afterwards withdrawn through lateral openings at the base, some of the material which is in a fine state of division falling through the fire-bars. In starting work with a furnace such as this the necessary quantity of fuel is placed on the fire-bars and the ore charged in upon it. Furnaces of this kind are, however,

only applicable to the roasting of ore or poor regulus in lumps. If the material is in too fine a state of division, the furnace soon becomes choked, air ceases to pass through it, and the roasting consequently comes to a termination. For ore or regulus in a fine state of division the Gerstenhöfer kiln may be employed. This kiln (figs. 1, 2) consists of a narrow vertical chamber, across which are placed numerous triangular iron or fire-brick bars. Supposing the furnace to be hot from previous working, the finely divided ore or poor



regulus is charged in through slits (c) in the roof of the furnace on to the base of triangular bars (u) placed below them. On these it heaps itself up and then falls over on to other bars still lower down. This operation is repeated again and again until the ore reaches a space free from bars at the bottom of the furnace. A current of air is simultaneously allowed to pass up through the furnace, and once the roasting is started, the heat produced by the combustion of the sulphur in the material treated is sufficient to cause the roasting to proceed by itself. Small holes (κ), which may be readily closed, are left in the front of the furnace, one on a level with the top of each transverse bar, and through these tools may be inserted, by the aid of which the ore that has collected on the bars may be removed. The current of air that is allowed to pass through the furnace is carefully regulated to prevent too great a dilution of the sulphurous acid produced by the combustion of the sulphur in the ore, this being usually conducted to sulphuric acid chambers. It is evident that if the material to be treated is readily fusible, as, for

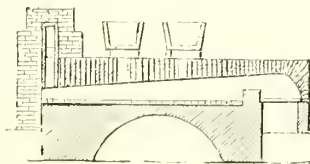


FIG. 3.

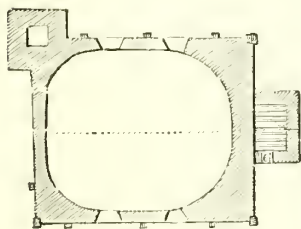


FIG. 4.

instance, rich copper regulus, it would clot together on the cross-bars, and would thus destroy the utility of the furnace. Such materials cannot therefore be roasted in this way, nor, indeed, by kilns at all. They may, however, be treated in reverberatory furnaces. The various modifications of these furnaces that are used for the roasting or 'calcination' of copper ores differ considerably from one another as regards their general construction, but they have one feature in common—the relatively small grate area as compared with the volume of the laboratory portion of the furnace.

According to Gruner (*Métallurgie*, 1, 269) the area of the fire-grate should not exceed 1 square foot for every 15 to 20 square feet of the laboratory portion of the furnace.

Figs. 3 and 4 show the general construction of this furnace.

The main distinctions existing between the various kinds of reverberatory furnaces consist in the methods of firing that are adopted, and in the arrangements connected with the

hearth of the furnace, this being sometimes fixed, sometimes made to revolve horizontally, and sometimes the laboratory portion of the ordinary reverberatory furnace is replaced by a cylinder which is made to rotate around a central axis. The reason for causing the laboratory portion to rotate or revolve is that by this means the ore on the bed may be stirred automatically and fresh surfaces be thus continually presented to the oxidising action of the furnace gases.

The sulphide ore, having been partially roasted by one or other of these methods, is then submitted to a fusion process with the intention of causing the silica either present in the material itself or added to the charge to combine with a certain portion of the iron also present to form a fusible iron silicate poor in copper, which may be thrown away, lime and other impurities being simultaneously slagged off. To avoid loss of copper in this process it is necessary to have a sufficient quantity of sulphur in the charge, and to this end fresh sulphide ore may be added, in which case the oxide of copper in the ore that has been roasted reacts with the iron sulphide in the added material, forming ferrous oxide, which combines with the silica to form a fusible slag, and a fused product consisting of the sulphide of copper so produced with the excess of iron sulphide intentionally left in the charge. This fused product is termed a 'regulus,' and as obtained in this stage of the process usually contains about 30 p.c. of copper. It should not contain more than some 35 p.c. of copper and a similar quantity of iron, though the percentages met with in practice are very variable. It is termed 'coarse metal,' 'metal' being the name given to a regulus in the Welsh method of copper smelting. The slag, 'ore-furnace slag,' is a mixture of mono- and bi-silicates, and ought not to contain more than 0.5 p.c. of copper. Various analyses show it to contain from 30 to 50 p.c. of silica, 17 to 36 p.c. of ferrous oxide, 2 to 16 p.c. of lime, and varying quantities of other constituents. The reverberatory furnace used in this fusion process differs from that employed for the previous roasting or 'calcination' of the ore, in that the area of the grate as compared with the volume of the laboratory part is considerably larger, owing to the higher temperature that must of necessity be employed. This ratio as given by Gruner is 1 : 5 or 6.

The next operation being a further calcination of the coarse metal produced in this process it is necessary to obtain it in a fine state of division, and it is therefore usual to run the molten regulus, as tapped from the furnace, into a tank filled with water, by which means it is obtained in a granular form. The finely divided regulus is then roasted as before, and is afterwards fused again for the production of another regulus richer in copper and poorer in iron than is the coarse metal obtained at the earlier stage of the process. To shorten the roasting period oxidised ores of copper are, when possible, added to the charge, and so, occasionally, are the slags rich in copper from succeeding operations. This, however, is not advisable, owing to the impurities these slags contain, which, in part at any rate, would pass into the 'blue' or

'white' metal resulting from this second fusion. It is desired to produce at this stage as pure a regulus as possible, and it is therefore customary, either by carrying the oxidising roasting farther than would otherwise be permissible, to allow the formation of a certain quantity of metallic copper (bottoms) into which most of the impurities, including gold and silver, will pass, or to place apart the first pigs of regulus that are tapped from the furnace, these pigs being similarly more impure than those succeeding them. This process is known as 'best selection.' The regulus, if it be 'blue metal,' will contain about 55 p.c. of copper; if it be 'white metal' the percentage of copper may reach as much as 75; whilst a still richer regulus containing much metallic copper, known from its appearance as 'moss' copper, bears the name of 'pimple metal' from the appearance of the surface of the cast ingot.

The next stage of this process consists in the partial oxidation of the regulus obtained by the previous operation, and then by raising the temperature to cause the oxide of copper formed by the roasting to react on the residual cuprous sulphide, forming metallic copper in the way already described. This process is termed 'roasting,' the previous oxidising stages of the process being, as has already been mentioned, termed 'calcination.' The products are an impure metallic copper, and a slag rich in that metal. This slag is either added to the previous fusion stages of the process or, owing to the impurities it contains, is treated by itself. The 'coarse copper' produced at this stage contains appreciable quantities of iron and other impurities and has to be 'refined.' This refining is based on the greater affinity shown for oxygen by the impurities present in the copper than is shown by the copper itself. The process is as follows:—The copper to be refined is charged on to the bed of a reverberatory furnace with a hearth area relatively larger than that employed in any of the previous stages, and is then slowly melted down in an oxidising atmosphere. The oxides formed in this manner are in part volatilised and in part combine with the silica of the furnace walls to form a highly basic scoria, which is frequently removed. As the impurities are oxidised away the copper itself begins to be attacked, and towards the end of this portion of the refining stage a layer of copper oxide formed on the surface of the bath reacts on the cuprous sulphide also present, forming metallic copper and sulphurous acid, which latter, on escaping, causes the bath of molten metal to 'boil.' When this ceases, the copper remaining on the hearth of the furnace contains large quantities of cuprous oxide. It is known as 'dry' copper. To remove this oxide the copper is then submitted to a reducing process. Poles of wood are thrust into the bath, and then anthracite or charcoal is thrown upon the surface of the molten metal. The products of the dry distillation of the wood stir up the molten bath and expel the sulphurous acid remaining dissolved in it after the boiling stage, at the same time partially reducing the oxide of copper also present, but this is chiefly removed at the second period of the operation when anthracite is thrown on the surface of the metal. Portions of the

metal are removed from the furnace from time to time, and when the metal is found to have lost its dark-red colour and granular fracture and to have become flesh-coloured, with a fibrous fracture and silky lustre, and to bend double when placed in the jaws of a vice, the refining is finished. The refined metal so obtained is not chemically pure, but contains variable percentages of different impurities. These would of themselves exert a deleterious influence on the copper, but it is found that this influence is neutralised by the simultaneous presence of a small percentage of cuprous oxide (tough-pitch copper rarely contains more than about 0.25 p.c. of oxygen). If either too much or too little of this oxide is present the metal will have lost its valuable mechanical properties, and will be useless for most purposes. If cast into an ingot the copper containing too much cuprous oxide will show a furrow along its surface, an ingot with the right proportion will have a flat surface, and one with too little will show a ridge. These different kinds are known respectively as 'dry' or 'underpoled,' 'tough-pitch,' and 'overpoled.' In the refining process, use is sometimes made of the fact that when one readily oxidisable metal is present its oxidation tends to induce less readily oxidisable metals also present to be oxidised with greater rapidity; lead is therefore frequently added, but it cannot be used when the copper is to be made into brass.

A modification of this reverberatory process consists in the use of blast furnaces for the fusion of the regulus.

## 2. THE REDUCTION PROCESS.

In this process either oxidised ores or ores which have been oxidised by a previous roasting, are melted down with the addition of coke or charcoal, usually in blast furnaces. This reduction also forms a distinctive feature in the German or blast furnace method for the treatment of sulphide ores. In this the operations are theoretically identical with those in the Welsh or reverberatory process just described, until the stage is reached at which the 'blue' or 'white' metal is converted into metallic copper. In the reverberatory process it has been shown that this is effected by the action of the oxide, produced by the partial oxidation of the sulphide, upon the residual sulphide; in the German method the sulphide is roasted completely to oxide and this is then reduced by carbon. The great objection to the use of this reduction process for the conversion of the regulus into metallic copper, is that a considerable percentage of copper passes into the slag, and as large quantities of this are formed owing to the necessary addition of fluxes to carry off the iron and other impurities, the loss of copper in this way is considerable. The copper, too, that is produced is very impure, and in refining it a larger percentage of copper passes into the slag than would otherwise be the case. If the slag is too rich in copper to admit of its being thrown away, it is melted with materials containing sulphur, the copper being separated in the form of a regulus in the ordinary way.

In the blast furnaces used for the treatment of copper ores, for that portion of the furnace in the neighbourhood of the tuyères where the

heat is greatest and the furnace walls most rapidly corroded, a hollow iron casting through which a current of water is caused to pass, is frequently employed in the place of the ordinary brickwork.

Besides these two main methods for the treatment of sulphide ores, there is one other which, though still in the experimental stage, may in the future prove of considerable importance. This process consists in the application of a modified form of the Bessemer converter in the treatment of copper regulus. A regulus poor in copper, such as the 'ore metal' previously described, would be first melted down and then charged in the molten condition into one or other of the various modified types of converter that have been proposed, and a current of air forced through the molten mass. The iron and other impurities are oxidised, and floating on the surface of the molten metal, attack the converter lining, forming slag, and a regulus is produced that is much richer in copper than the one originally charged into the converter, just as in the case of the ordinary copper process. The converter is then turned down and its contents either poured out altogether or the slag only is removed. In the former case the slag is separated from the regulus, which is then, if necessary, remelted, and is then returned to the same converter, or charged into another one, and the blast again turned on. The sulphur is in this way burnt away, and metallic copper remains behind in the converter, the heat of combustion of the sulphur maintaining the bath in a fluid condition. The great difficulty that has been experienced in working out this process practically, lies in the comparatively small amount of heat that is developed by the combustion of the sulphur in the bath, this not being sufficient to maintain the copper produced in a thoroughly molten condition in the presence of the cooling action of the blast passing through it. It was found that the metal was apt to choke the tuyères through which the air was introduced into the converter, and these had therefore to be placed in a different position from that which the high temperature developed on the combustion of the silicon and other impurities existing in pig iron enables them to occupy in the Bessemer converter as used for the production of steel. They were, therefore, removed from their vertical position in the bottom of the converter and placed more or less horizontally at the sides at some distance from the bottom. Again, it was found that the lining of the converter became rapidly corroded by the large quantities of ferrous oxide produced in the process, and this has had to be met either by modifying the character of the lining used, a more or less basic material replacing the acid ones previously employed, or by charging siliceous materials into the converter, and by not completing the conversion of poor regulus into metallic copper in one operation. The great advantage of the process consists in the great saving of fuel its effects as compared with either the reverberatory or blast furnace methods of treatment.

Besides these methods for the treatment of copper ores by the 'dry' way, there are others which involve the use of aqueous solutions. Wet methods for the treatment of copper ores

involve: 1. A conversion of the copper into a soluble form; 2. Its solution; and 3. Its precipitation. The soluble salts of copper which may be produced by simple metallurgical methods are the chlorides and the sulphate. These may be produced by direct solution in acids, or, as regards the sulphate, this is readily produced in the case of sulphide ores by a careful roasting, and in the case of oxidised ores either by the employment of sulphuric acid or by roasting in admixture with ferrous sulphate. If the material to be so treated contains the sulphides both of copper and iron, and it is submitted to a gradually increasing temperature in a reverberatory furnace, starting with the furnace cold and an oxidising atmosphere being maintained, it will be found that the iron sulphide either burns directly to iron oxide or is converted into the sulphate, which, however, is decomposed at a very low temperature. The final products of the roasting of the iron sulphide are ferric oxide and a mixture of  $\text{SO}_3$  and  $\text{SO}_2$ . The copper sulphide roasts to sulphate, and this does not decompose at so low a temperature as does the iron sulphate. It is consequently possible to convert the iron sulphate into insoluble ferric oxide while leaving the copper in the form of the soluble sulphate, any oxide of copper that may be formed being again converted into sulphate by the  $\text{SO}_3$  produced by the decomposition of the iron sulphate. The soluble copper sulphate may then be extracted from the roasted material by leaching it with water, and the copper in the solution may be precipitated either in the metallic state by the aid of some other metal, such as iron, or by the aid of an electric current, or in any other way. At some places hydrogen sulphide has been used for this purpose, but the precipitate is very bulky and rapidly oxidises. The metallic copper that is obtained by precipitation with iron is also rapidly oxidised by moist air.

The conversion of the insoluble copper sulphide or oxide into the soluble chlorides is effected either by roasting with salt, with or without the addition of iron sulphide or sulphate, or by treating the ore with hydrochloric acid or a soluble chloride such as ferrous chloride. When roasting with salt, the sulphates, decomposing, attack the salt, converting it in the presence of moisture into sodium sulphate with the evolution of hydrochloric acid, which in turn, aided by free chlorine also produced in the furnace, converts the oxides of copper present in the charge into cupric chloride, soluble in water, and cuprous chloride, soluble in brine. The copper may be precipitated from the aqueous solution so produced either by iron or lime. If iron is used it is advisable to pass a current of sulphurous anhydride through the solution to reduce the cupric chloride to cuprous chloride before the addition of the iron, a less quantity being in that case required for the precipitation of the copper. This reduction by sulphurous anhydride is utilised in the Hunt and Douglas process, in which the solvent employed for oxidised ores is ferrous chloride.

These wet processes for the treatment of cupriferous materials owe their importance to a great extent to the facilities they afford for the collection of any silver that may be present



in the ore or metallurgical product to be treated, and their treatment belongs rather to the metallurgy of silver than to that of copper.

The electrolytic process is applicable both to the treatment of copper ores and of copper regulus, as well as to the refining of the pure copper. It is usually employed for this latter process, rarely for the treatment of regulus, and still less frequently for the treatment of ore.

Of the ores of copper, the following sulphides are good conductors of electricity: Redruthite, Bornite, and Copper pyrites.

Cuprite, Azurite, Malachite, Dioptase, and Fah-Ore, are either bad or non-conductors. If, therefore, it is desired to treat these latter ores electrolytically, they must either be converted by metallurgical treatment into a state in which they conduct electricity before employing them as the anode or dissolving pole of the copper bath, or this anode must be formed of some conducting material, such as coke, and the ore placed around it. This, again, is only possible when the ore is readily attacked by the (SO<sub>2</sub>) evolved on the anode surface during the passage of the current of electricity through the bath. A copper regulus, on the other hand, is a good conductor, and may be cast in the form required for the anode. Its treatment, however, involves some difficulty, owing to the fact that the solution of the regulus proceeds not only on its outer surface, but, in places, throughout its mass. Owing to this fact the regulus, after being in the bath for a time, gradually softens and falls to pieces. It has therefore to be supported. This is usually effected by casting the regulus around a copper plate, which is protected in those places where it is subject to the dissolving action of the bath by a coating of wax or other similar material. Again, when regulus is employed as the anode, some of the sulphur it contains escapes in the form of hydrogen sulphide, which in part precipitates the copper from the solution with which it comes in contact, and in part escapes altogether from the bath. This necessitates the employment of complicated arrangements to prevent the escape of the gas into the atmosphere of the works, and complicates generally the electrolytic treatment. The large quantity of iron, too, that is present in the regulus soon renders the working solution so rich in iron as to become useless for the purpose for which it is employed, and the cost of treatment is considerable. Still, it has been employed occasionally with some success.

The electrolytic process, however, is chiefly employed in the refining of impure copper, and is especially applicable to the treatment of impure copper 'bottoms' containing gold and silver. The method employed is briefly as follows. The impure copper that is to be treated is cast in the form of slabs, copper hooks being inserted into the copper while still molten. These slabs of impure copper form the anodes or dissolving poles. The vat or tank in which the electrolytic treatment is to take place is usually made of wood lined with sheet lead. Instead of lead, however, any other material which will resist the action of the acid solution that the tank is to hold may be employed, and, as far as the protection of the vat itself

is concerned, a mere tarring is to some extent sufficient. This, however, is unsuitable, as it leads to the deposition of metallic copper on the walls of the tank. If the tank is lined with lead, this again must be protected from accidental injury by an inner lining of matchboarding. The sides of the tank must be of sufficient strength to withstand the outward pressure of the solution and the crushing strain of the copper anodes, cathodes, and conducting rods resting upon them. Tie-rods are usually employed to add to the strength of the tank. The size of the tanks employed varies greatly, but one that is somewhat common has a depth of 3 feet 6 inches and a breadth of about 4 feet. The tank rests on wooden trestles for the purposes of isolation. At one of the sides of the tank are placed the two main conducting rods, one above the other; the other copper rods are laid across the tank, resting at one side on one or the other of the main conducting rods, and at the other on wood or some other non-conducting material. These form the supports for the anodes and cathodes. The ends of the bars resting on the main conducting rods are hooked to prevent them slipping. They may be made hollow, with iron rods inserted in them to give the necessary strength. The impure copper anodes are hung from one set of these bars, and, their weight being considerable, no special precautions have to be taken to ensure contact. Facing a row of anodes is a row of cathodes. These latter, being formed of thin sheet copper, do not of themselves possess sufficient weight to ensure adequate contact with the cross-bars on which they rest, and they have therefore to be attached to these by the aid of wire. The distance apart of the several rows of cathodes and anodes is usually about two inches, but this depends on the strength of the current, the nature of the bath, the purity of the copper, and the method of working generally. The anodes reach to within about 4 inches of the bottom of the tank, this space being left to admit of the deposition of the impurities separated during the solution of the impure copper. The bath consists of an acid solution of copper sulphate, containing about  $\frac{1}{2}$  lb. of sulphuric acid and  $1\frac{1}{2}$  to 2 lbs. of copper sulphate to the gallon. This solution, being liable to separate into layers of different density, must be kept in constant motion, not violent enough, however, to prevent the mud depositing itself properly without being carried forward towards the cathode, to the face of which it would immediately adhere. This is effected either by the aid of pumps made of hard lead, or by so arranging the baths that the solution will flow from the bottom of one tank to the surface of another by a syphon action, a difference of level of about 3 inches being usually sufficient for this purpose. On the first introduction of the electrolytic process for the refining of copper, large tanks and electric currents of low electromotive force were employed. Now the converse is usual, a large number of the tanks being connected in series.

With the exception of silver and gold, the various metallic impurities present in commercial copper pass into solution before the copper on the electric current being passed through the anode, and, inversely, with careful working,

copper may be deposited on the cathode before those elements which passed first into solution. As silver is almost insoluble in the dilute sulphuric acid bath employed in this process, it falls with the gold to the bottom of the tank in the form of a mud, together with other impurities. It is evident, therefore, that not only does the electrolytic process permit of the production of copper of a high degree of purity, but it also affords a means for the separation of the silver and gold present in the copper ore originally treated. Owing to the large quantity of copper under treatment, as compared with the production of the refined copper, the process is somewhat costly, and Fontaine is of opinion that under favourable conditions the cost of refining the ton of copper by this process cannot be much less than 6*l.* per ton.

The purest copper that can be obtained commercially has nearly as low a resistance to the passage of an electric current as silver. This resistance is, however, greatly increased by the presence of traces of other elements. The mechanical properties of copper are also influenced in a similar manner; the presence of minute quantities of arsenic or antimony being very deleterious. The specific gravity of copper is about 8.96. The total production of copper in 1887 was about 225,000 tons.

The alloys of copper are of great importance, brass being a copper-zinc alloy; speculum metal, bell-metal, and gun-metal, alloys of copper and tin; bronze, an alloy of copper and tin, with or without the addition of zinc or lead; German silver an alloy of copper, zinc, and nickel; and delta metal an alloy of copper, zinc, and iron. Brass usually contains about 2 parts of copper to 1 of zinc; gun-metal 91 of copper and 9 of tin; bell-metal 78 of copper, and 22 of tin.

#### THE ASSAY OF COPPER ORES.

There are two main methods employed in the assay of copper ores. These involve the use of (1) fusion methods, and (2) wet methods.

*Fusion methods.*—There are two processes belonging to this class: (1) the German, and (2) the Cornish. The German method consists in roasting the copper ore until the whole of the copper is present in the form of oxide; then fusing this with fluxes and a reducing agent for the production of an impure copper; and then refining the impure copper so obtained. The Cornish method is employed for the treatment of sulphide ores, and resembles the Welsh method of copper smelting. It consists in fusing the ore with the addition, when necessary, of iron and sulphur for the formation of a copper regulus, containing about 50 p.e. of copper; then roasting this regulus to oxide; subjecting the roasted ore to a reducing and fluxing fusion for the formation of metallic copper, and then refining the resulting impure copper so obtained.

Both methods yield very inaccurate results. The Cornish method is, however, still of considerable commercial importance, and is briefly as follows, the treatment depending on the percentage of sulphur present in the ore. Copper ores are, therefore, divisible into two main classes, (1) *yellow* ores containing more sulphur

and iron than is necessary for the conversion of the whole of the copper present into a regulus containing 40-60 p.e. of copper, and (2) *grey* ores containing less than the necessary percentages. There is also an intermediary class of which purple copper ore is an example.

The quantity of ore taken for the assay is as follows:

Percentage of copper	Weight of ore Grains
10 . . . . .	400
10-30 . . . . .	200
Over 30 . . . . .	100

The necessary quantity of the ore, powdered to such a degree of fineness that it will pass through a 60-mesh sieve, is mixed thoroughly with the necessary quantities of flux, the following being examples:

	Ore Class I. Grains	Ore Class II. Grains
Ore . . . . .	200	100
Nitre . . . . .	50	—
Lime . . . . .	200	200
Fluorspar . . . . .	200	200
Glass . . . . .	150	150
Borax . . . . .	150	150
Sulphur . . . . .	—	20
Hamatite . . . . .	—	30
Tartar . . . . .	—	30

The mixture is then fused in a clay crucible for about 15 minutes at a rather low temperature and the contents are then poured into an iron mould. While still hot, the button of regulus and slag is dipped for a moment into water to facilitate the separation of the regulus from the slag. When cold, the regulus is carefully broken off and the slag powdered and examined for shots of regulus. It may prove necessary to fuse the slag again to ensure the complete separation of the regulus. The regulus is then powdered, placed in a clean crucible and roasted carefully, commencing at a very low temperature and stirring continuously. The temperature should be high towards the end for the purpose of decomposing any sulphates that may be formed. The roasted regulus is then fused for coarse copper in the same crucible as that in which the roasting was effected, the following mixture being employed:

	Grains
Tartar (Argol) . . . . .	50-150
Sodium carbonate . . . . .	50-150
Borax . . . . .	20-30

This is fused for about 15 minutes. The contents of the crucible are then poured, the button of slag and metal dipped into water, and the button of copper separated when cold from the slag. The slag is then powdered and fused again with the following mixture:

	Grains
Tartar . . . . .	50
Charcoal . . . . .	5
Sodium carbonate . . . . .	20

The bead of copper obtained is added to that resulting from the previous fusion. The temperature of the furnace is then raised as high as possible, and the crucible used in the previous operation placed in the fire. When the temperature of the crucible has exceeded the melting-point of copper, the copper to be refined is

placed in it. The copper melts, and the foreign metals present in the button, being oxidised away before the copper is attacked, cloud the surface of the molten metal. When the oxidation of the impurities is complete, the film clears away, leaving the surface of the metal bright. About 100 grains of refining flux (produced by mixing together 3 parts by volume of powdered nitre,  $2\frac{1}{2}$  parts of tartar, and 1 part of salt, and then deflagrating the mixture by inserting a red-hot iron) is then rapidly thrown into the crucible, fusion is maintained for about 2 minutes, and then the contents of the crucible is poured out, the button of metal examined, and weighed if the refining has been properly effected. The slag contains some copper, and this is subjected to a reducing fusion as before.

*Wet methods.*—The wet method chiefly in use for the assay of copper ores consists in titrating the ammoniacal solution of the ore with potassium cyanide until a colourless solution results.

The standard solution used is obtained by dissolving 20 grams of pure potassium cyanide in one litre of water. If the ore to be assayed for copper is completely decomposed by acids, it is dissolved in the ordinary way, but when silicate of copper is present, as in the case of slag, the material must either be fused with sodium carbonate or treated with hydrofluoric acid. The acid solution of the ore is treated with an excess of ammonia and ammonium carbonate, and titrated till colourless with the standard solution of cyanide. It is customary to make several assays simultaneously, the same interval of time being allowed to elapse between the commencement and completion of each assay and of the standardising solution treated at the same time, the decolourising effect of the cyanide not being instantaneous. The solution is titrated in a flask, the contents of which is kept in constant motion. If iron is present in the material to be assayed it should be carefully removed, or a similar quantity should be added to the solution used for standardising.

In the electrolytic method the ammoniacal solution of the copper obtained as above is acidified with nitric acid, placed in a weighed platinum dish, and a current is passed through the solution from two Daniell cells arranged in series by the aid of a platinum wire dipping into it, connected with the copper pole of the battery. The platinum dish rests on a piece of copper connected with the other pole of the battery, and the copper is deposited on it. When the deposition of the copper is complete it is washed with water without breaking the current, then with alcohol, and finally with ether. It is then dried in an air-bath and is afterwards weighed, the difference in weight before and after the passage of the current representing the weight of the copper.

Another wet method, one of very considerable accuracy, that is employed for the determination of the percentage of copper in alloys is the following. Make a standard solution of sodium hyposulphite by dissolving 37 grams in 1 litre of water; then make a solution of starch containing about 0.3 gram in 1 litre of water.

Dissolve 0.3 gram of the alloy in nitric

acid, dilute to about 100 c.c., add a concentrated solution of sodium carbonate until a slight precipitate is produced, then dissolve in a slight excess of acetic acid, add 2 grams of potassium iodide, and titrate with the standardised solution of sodium hyposulphite, some starch solution being added to determine the reaction. The titration must be effected immediately after the addition of the potassium iodide and the solution must not be too dilute. Ferrie salts and all substances which decompose potassium iodide must be absent. If iron (arsenic &c.) is present in the alloy to be assayed, the solution must be first treated with sulphuretted hydrogen before titrating it.

*Literature.*—The following are among the principal modern text-books relating to this subject:—E. D. Peters, *Modern American Methods of Copper Smelting*, New York, 1887; J. A. Phillips and H. Bauermann, *Elements of Metallurgy*, London, 1887; A. Classen, *Quantitative chemische Analyse durch Electrolyse*, Berlin, 1886 (French translation by C. Blas, Paris, 1886); H. M. Howes, *Article on Copper Smelting*, Bulletin of the U.S. Geological Survey, No. 26, 1885; A. F. Wendt, *Pyrites Deposits of the Alleghenies*; C. A. Balling, *Grundriss der Elektrometallurgie*, Stuttgart, 1888; *Die Metallhüttenkunde*, Berlin, 1885; *Metallurgische Chemie*, Bonn, 1882, and *Probirkunde*, Brunswick, 1879 (French translation of the *Assaying* by L. Gautier, Paris, 1881); Bruno Kerl, *Allgemeine Hüttenkunde*, and *Grundriss der Metallhüttenkunde*, Leipzig, 1881; *Metallurgische Probirkunde*, Leipzig, 1882 (English translations of smaller book on *Assaying* by J. Brannet, London, 1883, and, with additions, by F. Lynwood Garrison, Philadelphia, 1889); H. Fontaine, *Electrolyse*, Paris (English translation by J. A. Barly, London, 1885); W. Crookes, *Mitchell's Manual of Practical Assaying*, London, 1881; M. L. Gruner, *Traité de Métallurgie*, Paris, 1875, 1878; J. Percy, *Metallurgy*, 1, 1861 (with article on *Assaying* by Mr. Richard Smith). See also the *Bibliographies* appended to the works of Balling and of Bruno Kerl.

#### COMPOUNDS OF COPPER.

*Oxides.* Four distinct oxides of copper are known; the quadrantoxide  $\text{Cu}_2\text{O}$ , the sub- or hemi-oxide  $\text{Cu}_2\text{O}$ , the monoxide  $\text{CuO}$ , and the peroxide  $\text{CuO}_2$ . An oxide  $\text{Cu}_3\text{O}_2$  (Maumené) and others intermediate between the suboxide and the monoxide are also said to exist.

Copper suboxide, or hemioxide, red oxide of copper, cuprous oxide  $\text{Cu}_2\text{O}$ , occurs native as *cuprite* or red copper ore and as *chalcotrichite*.

It may be prepared (1) by heating finely divided copper in air below a red heat; (2) by gently heating a mixture of 5 parts cuprous chloride and 3 parts sodium carbonate in a covered crucible and separating the oxide by lixiviation; (3) by reduction of an alkaline solution of a copper salt by sugar or certain other organic bodies, as in Fehling's sugar test; (4) by heating in a covered crucible a mixture of 5 parts copper monoxide and 4 parts copper filings.

This oxide is decomposed by most acids into a cuprie salt and copper; hydrochloric acid, however, converts it into cuprous chloride.



Cuprous oxide fuses at a bright red heat. It dissolves in metallic copper and renders it brittle or 'dry' when present in quantity. As much as 4.6 p.c. has been found by Abel in very dry copper, and, according to Watson (S. C. I. 1883, 154) from 1 to 2½ p.c. is present in ordinarily good copper.

It is largely used for the production of *ruby glass*, and together with the black oxide forms one of the so-called *copper paints* used for painting ships' bottoms.

The hydrous oxide is produced by the action of alkali on cuprous chloride. It is a powerful reducing agent, especially in ammoniacal solution. This solution, which is colourless, immediately becomes blue from the formation of the monoxide on exposure to the atmosphere, and thus forms a delicate test for oxygen. The hydrous oxide dissolves in a concentrated solution of magnesium chloride.

**Copper monoxide, cuprous oxide, black oxide of copper, 'cupper oxide'**  $\text{CuO}$ , occurs as *melanconite* or *black copper*, especially at Lake Superior.

It may be prepared by heating the nitrate or carbonate to dull redness or the sulphate to intense redness. The copper oxide used for organic analysis &c. may be prepared by moistening copper scale (the mixture of suboxide and black oxide obtained while working copper sheet &c.) with nitric acid, and igniting.

Copper oxide is a black powder which agglomerates when heated and fuses at the melting-point of copper with evolution of oxygen, leaving a residue containing  $\text{CuO} \cdot 2\text{Cu}_2\text{O}$ . It is slightly hygroscopic, especially when in powder. When heated with organic substances or certain gases, it is reduced to metal. The metal produced by reduction in hydrogen always contains that gas, but if the oxide be reduced in formic acid vapour the metal is quite free from hydrogen and is very suitable for organic analysis (Weyl, B. 15, 1139).

It dissolves in acids with formation of cupric salts. In oils &c. it is soluble to some extent; it is for this reason that copper cooking vessels require such constant cleansing.

Copper oxide is used for ultimate organic analysis; to make green and blue glass, and to some extent, as a pigment. It has also been used as one electrode of a galvanic cell (v. Lelande and Chaperon, Bl. [2] 40, 173).

**Hydrated copper oxide**  $\text{CuO} \cdot \text{H}_2\text{O}$  may be prepared by precipitating a solution of a copper salt by addition of alkali and washing rapidly. When heated with water it becomes black and amorphous. The hydrated oxide dissolves in ammonia, the saturated solution in strong ammonia being known as 'Schweitzer's reagent.' This solution, which may also be prepared by exposing copper turnings partially covered with ammonia to the air, has the property of gradually dissolving *cellulose* with formation of a viscid solution. The 'Willesden papers' are prepared from solution of cellulose in ammoniacal solution of copper or zinc oxides (v. CELLULOSE).

The hydrated oxide is also used as a blue pigment by paper-stainers, but becomes green on exposure. It corresponds closely with certain of the highly basic carbonates sold as *verditer*,

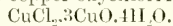
According to Dumas it is best prepared as follows: 6 parts of copper sulphate are dissolved in water and mixed with a solution of 3 parts of calcium chloride. The clear liquid is decanted from the precipitated calcium sulphate and is mixed with 1½ parts of lime made into a cream with water. The greenish precipitate is collected, washed, and mixed with one-fourth its weight of slaked lime and as much pearl ash, and to render the colour more permanent, one-fourth its weight of ammonium chloride and one half its weight of copper sulphate are usually added.

**Salts.** Two series of copper salts are known, *cuprous* and *cupric*. The former are mostly insoluble in water, and are of but little commercial importance. They act as powerful reducing agents and readily pass into the cupric condition. Cupric salts are mostly soluble, and are of wide application.

**Cuprous chloride**  $\text{Cu}_2\text{Cl}_2$  may be prepared, amongst other methods, by boiling cupric chloride with hydrochloric acid and copper turnings. On addition of water it is precipitated in white crystals.

It melts below a red heat into a yellow transparent mass. The dry crystals become yellowish on exposure to light; if moist they acquire a dirty violet tinge. Plates of copper coated with this chloride by the action of chlorine will take photographic impressions, but cannot be made to withstand exposure to light (v. Carlemann (J. pr. 63, 475) and Priwoznik (D. P. J. 221, 38)).

The hydrochloric acid solution, when exposed to air, absorbs oxygen and acquires a brown colour, subsequently depositing a pale bluish-green insoluble copper oxychloride



An identical substance used as a pigment, and known as *Brunswick green*, is prepared by boiling a solution of copper sulphate with a small quantity of bleaching powder solution, or by moistening copper turnings with hydrochloric acid or ammonium chloride with free exposure to air. It occurs in nature as *atacamite*.

**Cuprous sulphide**  $\text{Cu}_2\text{S}$  occurs as *chalcocite* or *copper glance*. It may be prepared by heating copper to redness in sulphur vapour, or by heating a mixture of copper and sulphur. It has no commercial application.

**Cupric chloride**  $\text{CuCl}_2$  may be prepared as a fused, liver-coloured, anhydrous mass by heating copper in excess of chlorine. In solution it may be prepared by dissolving the oxide in hydrochloric acid. It crystallises in grass-green prisms or needles containing 2 molecules of water. They become pale blue when dried *in vacuo*.

Cupric chloride is very deliquescent and is soluble in alcohol. When a small quantity of potash is added to the aqueous solution, a pale blue basic oxychloride  $2\text{CuO} \cdot \text{CuCl}_2 \cdot 4\text{H}_2\text{O}$  is precipitated. It turns to a black anhydrous powder when heated, but again becomes green with absorption of 3 molecules of water when moistened. It is an intermediate product in the manufacture of *verditer* (v. *Copper carbonates*).

Cupric chloride is used in calico printing, in the manufacture of *methyl violet*, and for the oxidation of *Cutch colours*.

**Cupric sulphate**, *Blue vitriol*  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . This salt may be prepared by dissolving copper or its oxide in sulphuric acid.

It is prepared on the large scale from metallic copper in the following way. Old copper plates from the sheathing of ships &c. are heated to strong redness in a reverberatory furnace and an excess of sulphur is thrown in and the doors are closed. When combination is complete, the doors are re-opened and the heat is raised to dull redness to oxidise the sulphide into sulphate. The mass, while hot, is thrown into dilute sulphuric acid, allowed to settle, decanted, concentrated, and crystallised. The sulphate so produced is of considerable purity.

*Coarse copper* and *copper glance* or other sulphurous copper ores are similarly treated. When much iron is present, as in most copper ores and especially in copper pyrites, it would be impossible to separate the copper and ferrous sulphates by crystallisation, because, although copper sulphate crystallises normally with 5 molecules of water, it forms, in presence of ferrous sulphate, crystals isomorphous with that salt and containing 7 molecules of water. By carefully adjusting the temperature at which the sulphide is roasted, however, the iron salt may be converted into the oxide while the copper sulphate remains almost unaffected. The iron may be oxidised and thus separated from the copper by boiling the solution with a little nitric acid. It may also be precipitated as oxide by boiling with copper oxide or by boiling with lead peroxide with subsequent addition of a little barium carbonate.

When the sulphate is required for purposes where the presence of iron is not injurious, such liquors, or the mother-liquors from which the purer salt has been separated, may be at once crystallised out with the formation of crystals containing both iron and copper. The '*agricultural copper sulphate*' is of this class. The '*Salzburg vitriol*,' prepared at Buxweiler, also contains both iron and copper. According to Lefort (C. R. 26, 185), it consists of  $\text{CuSO}_4 \cdot 3\text{FeSO}_4 \cdot 28\text{H}_2\text{O}$ . '*Cyprian vitriol*,' prepared at Chessy from zinciferous copper ores, forms blue rhombic prisms, which contain, according to Lefort,  $\text{CuSO}_4 \cdot 3\text{ZnSO}_4 \cdot 28\text{H}_2\text{O}$ .

The copper may be separated from the ferrous mother liquors by placing them in vats containing iron plates upon which the copper is slowly deposited.

This metal or other copper may be oxidised in a reverberatory furnace and dissolved in dilute sulphuric acid. If copper be known to contain silver or gold, as is the case with that from the Harz, it is treated with sulphuric acid diluted with its own volume of water, the copper being thus dissolved while the silver and gold are unattacked.

Argentiferous copper ores are roasted in a reverberatory furnace and added in small charges to sulphuric acid and digested until the solution contains but little free acid. The solution is then decanted from the precipitated lead and gold, and is concentrated and run into lead-lined tanks containing plates of copper upon which all the *silver* and part of the *antimony* and *arsenic* are deposited, while the greater proportion of the *bismuth* is precipitated as a basic

sulphate and the iron is reduced to the ferrous condition. The liquor is then crystallised, the mother liquors being used for treating a fresh quantity of ore. Copper sulphate is obtained of great purity and in considerable quantity in the refining of silver by precipitating it upon plates of copper from its solution as sulphate (*v. SILVER*).

Copper sulphate crystallises in large transparent blue, doubly oblique rhombic prisms of sp.gr. 2.28 and containing  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . According to Poggiale their solubility in 100 parts of water is

10°C.	20°	30°	40°	50°
36.59	42.31	48.81	56.9	65.83
70°	80°	90°	100°	
94.60	118.0	156.44	203.32	

When heated to 100° it loses 1 molecule of water and effloresces to a bluish-white powder; at 220° to 240° it becomes anhydrous, white, and hygroscopic, and combines with water with considerable heat. The sp.gr. of the anhydrous salt is 3.606 (Thorpe and Watts). The anhydrous salt combines with water in alcohol and other organic liquids with production of a blue colour, and may be used for ascertaining the presence of water in those substances, but the test is not delicate. The anhydrous salt is also soluble in *anhydrous* methyl alcohol, and produces a bluish-green solution (Képl., J. pr. 25, 526).

Copper sulphate absorbs hydrochloric acid gas with evolution of heat, forming cupric chloride and liberating sulphuric acid. It is therefore used to remove hydrochloric acid from such gases as chlorine or carbon monoxide. A similar reaction occurs in solution.

When mixed in solution with molecular proportions of potassium and other sulphates, it produces well-defined, crystalline double sulphates. Several basic sulphates are known.

The sulphate is the most important of the copper salts. It is largely used in calico printing, principally in connection with potassium bichromate or iron mordants; in black dyeing with logwood; directly or indirectly for the preparation of most pigments containing copper; to prevent rot in timber. In agriculture the crude sulphate containing ferrous sulphates is used to a considerable extent to prevent smut in seeds. The seeds are soaked for some hours in a weak solution of the sulphate, and are sown within twenty-four hours. A 10.20 p.c. solution of copper sulphate, preferably mixed with lime, is applied to vines with great benefit. A small quantity is found in the vines and must, but the tannin and sulphur introduced before fermentation appear to remove it, its presence in *wine* not having been definitely proved (*v. Muntz*, C. R. 101, 895, and Millardet and Gayon, C. R. 101, 924, and 985).

**Cupric nitrate**  $\text{Cu}(\text{NO}_3)_2$  may be prepared by dissolving copper or the oxide or carbonate in nitric acid. The solution at temperatures above 20°C. deposits dark-blue crystals containing 3 molecules of water, which melt at 114.5° and boil at 170° with evolution of nitric acid and formation of a green basic salt. This basic salt may also be prepared by boiling the solution of the nitrate with copper or copper hydrate, or with a little alkali (*v. also Copper carbonates* for an application of the basic nitrate).

Copper nitrate is used to a slight extent in dyeing and calico printing.

**Copper acetate** *v.* *Metallic acetates*, art. ACETIC ACID.

**Copper arsenite** *v.* *Scheele's green*, art. ARSENIC.

**Cupric phosphate** is of no technical interest. A brilliant green colour containing a basic phosphate, prepared by printing a mixture of copper acetate, sodium phosphate and ammonia has, however, been used for calico printing (Bourcart, *Monit. Sci.* [3] 4).

*Phosphorus* combines in several proportions with copper, and produces true alloys, which in many cases are of exceptional value.

**Cupric sulphide**  $\text{CuS}$ , occurs as *covellite* or indigo copper in blue flexible plates, in Vesuvian lava, in Chili, and in the copper mines of Mansfeld. It may be prepared by heating cuprous sulphide with sulphur at a temperature not above the boiling-point of sulphur; by digesting cuprous sulphide with cold strong nitric acid; by precipitating a copper solution with sulphuretted hydrogen. On the large scale it is obtained as a paste by precipitating a solution of the sulphate with sodium sulphide. This paste is used in calico-printing for the development of aniline black.

**Copper carbonates.** The normal salt has not been prepared, but several basic carbonates are known, and used as blue and green pigments. Basic copper carbonate occurs native as *malachite*  $\text{Cu}(\text{HO})_2\text{CuCO}_3$ , and as *azurite* or *chessylite*  $\text{Cu}(\text{HO})_2 \cdot 2\text{CuCO}_3$ . When ground these minerals form a fine but expensive pigment.

An anhydrous basic carbonate is precipitated on addition of a solution of sodium carbonate to a hot solution of copper sulphate or nitrate.

Under the names *Verditer green*, *Verditer blue*, *Bremen green*, and *Bremen blue*, this salt is largely prepared for paper-staining &c. According to Habich (*Technologiste*, 17, 413), the following processes are in use. A hundred parts of old copper sheathing from which impurities, oxide, &c., have been removed by digestion in dilute sulphuric acid, is cut into pieces and mixed with a paste formed by moistening a mixture of 99 parts potassium sulphate and 100 parts common salt, and the mixture is stirred occasionally for some months to ensure thorough exposure to the atmosphere. The action appears to consist in the production of cupric chloride, which in presence of the metal becomes converted into a basic chloride, and finally, by the action of the oxygen, into an oxychloride. If the oxidation be incomplete, the subchloride is not completely oxidised, and as it, when subsequently decomposed by alkali, gives an orange-red precipitate of suboxide, the pigment would be lowered in value. The oxychloride may also be similarly prepared from a mixture of 100 parts copper, 60 parts common salt, and 30 parts strong sulphuric acid diluted with three times its volume of water; or by treatment, with free atmospheric exposure, of copper with a solution of cupric chloride in hydrochloric acid.

To 100 kilos. of this thick magma of oxychloride, which has been washed by decantation, a concentrated solution containing 7 kilos. copper sulphate and 40 kilos. concentrated soda solution ( $32\text{--}36^\circ\text{B}$ .) is added. The mixture is vigo-

rously stirred and poured at once into 150 kilos. of soda solution ( $20^\circ\text{B}$ .). The precipitate is washed, passed through a fine hair sieve, and dried spontaneously or at a temperature below  $78^\circ\text{F}$ . If hot air be used in the drying, it must be quite free from acid or sulphur gases. To produce the finest colour, desiccation must be perfect.

Habich recommends the following process for making a *verditer* which has a very different composition from the above. A solution of copper oxide in nitric acid is treated with potassium carbonate, which is added in portions until most, but not all, the copper has been precipitated. The green precipitate is washed and introduced into a solution of copper nitrate whereby it is converted into a heavy green insoluble basic nitrate. This is digested in a solution of potassium zincate (formed by dissolving zinc in caustic potash solution). A dark-blue pigment, of great 'body' but little weight, is thus produced. It contains zinc and copper, apparently combined as a double oxide or as 'copper zincate,' and a small quantity of basic copper nitrate. The by-product from this process, potassium nitrate, is also valuable.

Verditer may be prepared by agitating a solution of copper nitrate with chalk. The washed pasty precipitate is mixed with 8-10 p.c. of freshly burnt lime with production of a fine velvety blue pigment. The precipitate without addition of lime is green.

According to Gentele, the following process is adopted at Bremen, Cassel, &c. 225 lbs. sea salt and 222 lbs. blue vitriol, both free from iron, are mixed dry and ground between millstones with water, to a thick paste. This paste is mixed in strata with 225 lbs. of clean copperplate cut into pieces about one inch square, in wooden chests made without nails, and the mixture is digested for about three months with the maximum exposure to air, the whole being well mixed and exposed about once a week. When the action is complete, the undissolved metal is removed and the precipitate is washed with a minimum of water, filtered and thrown into a tub. To 180 lbs. of the magma 12 lbs. of hydrochloric acid ( $13^\circ\text{B}$ .) is added, and the mixture is stirred and left for 24 or 36 hours. Six volumes of this solution is mixed with 15 volumes of caustic alkali ( $19^\circ\text{B}$ .) followed after an interval by 6 volumes of water. The mass is well mixed and left for 36-48 hours, and is then well washed by decantation, filtered, exposed for some time in a moist condition to the air, and finally dried (*v.* also *Copper monoxide*).

**COPPER GLANCE.** *Cuprous sulphide* *v.* COPPER.

**COPPER PAINT** *v.* COPPER.

**COPROLITES.** Concretionary mixtures of calcium phosphate and calcium carbonate, derived from the excrements of certain extinct fishes and reptiles. Formerly much used in the manufacture of superphosphate of lime (*v.* MANURE).

**CORAL** is the calcareous substance secreted by many varieties of four kinds of organisms, viz. (1) *Actinozooids*, the principal creators of coral reefs; (2) *Hydrozooids*, of the group of aculephs, makers of the large common corals known as millepores; (3) *Bryozoans*, producing



delicate corals in various forms, resembling mosses, branches, thin filamentary deposits, or more solid masses [in the Palaeozoic limestone formation this species of coral abounds]; (4) *Nullipores*, which, although closely resembling millepores, are veritable algae or sea-weeds; they may be readily distinguished from the millepores by the absence of perforations.

Coral is simply a secretion corresponding to the bone of vertebrates or the shell of mollusca, and is composed almost entirely of calcium carbonate derived from sea-water and from the food of the coral-making polyps.

Ordinary coral is somewhat harder than limestone or marble, and, when tapped with the hammer, gives out a ringing sound clearer than is elicited from ordinary calcium carbonate. The sp.-gr. of fifteen specimens examined by Silliman, averaged 2.523.

#### Composition of Coral.

S. P. Sharples (Am. S. 31, 168) found

—	Calcium carbonate	Calcium phosphate	Water and organic matter
<i>Oculina arbuscula</i> , N. Carolina . . .	95.37	0.84	3.79
<i>Mancinia arolata</i> , Florida . . .	96.54	0.50	2.96
<i>Agaricia agaricites</i> , Florida . . .	97.73	0.53	1.64
<i>Siderastraea radians</i> , Florida . . .	97.30	0.28	2.42
<i>Madrepora cervicornis</i> , Florida . . .	98.07	0.32	1.93
<i>Madrepora palmata</i> , Florida . . .	97.19	0.78	2.81

Small and variable quantities of magnesium carbonate, calcium sulphate, calcium fluoride, alkaline chlorides, silica, and oxide of iron are found in corals.

The red coral, *Corallium rubrum*, varies in colour from crimson to rose, the latter being the rarest and, therefore, the most prized. It is gathered from the rocky bottom and shores of the Mediterranean; and it occurs most abundantly at a depth of 25 to 50 feet; although, according to Dana, it may be found as deep as 1,000 feet. Forehammer found 2.1 p.e. magnesia in *Corallium rubrum*, and 6.36 in *Isis hippuris*. According to Trommsdorff, the red pigment of coral is a resin soluble in oil of turpentine, and, after removal from the coral by this solvent, is easily soluble in alcohol and ether, but insoluble in caustic potash. In a red madrepora, Vauquelin found a red colouring-matter which was turned violet by alkalis. Moseley has described in some corals and allied organisms a red colouring-matter (*Polyporphyrin*) which is insoluble in water, glycerine, alcohol, ether, and in strong solutions of ammonia and potash. It is soluble in moderately strong sulphuric, nitric, or hydrochloric acids. For the formation and distribution of coral and coral-reefs see *v. Corals and Coral Islands*, J. D. Dana; *Coral-reefs*, Darwin; Murray, in *Proc. R. Soc. Edinb.* 1880, p. 505. *V.* also Forehammer (J. pr. 49, 52; J. 1847, 1291; 1849, 813; 1851,

865; 1852, 958-961); Sharples, *loc. cit.*; Moseley, *Qu. Journ. Microscop. Sci.* vol. xvii. 1877.

#### CORALLINE *v.* ALGINE.

**CORDIALS and LIQUEURS** are compounds of weak spirit sweetened and flavoured with spices, fruits, or other substances. The fruit-essence which it is desired to use having been obtained by distillation, it is added to a syrup of the sugar and spirit. The spirit must be 'silent,' *i.e.* of so great purity as not to betray its origin, otherwise the flavour is impaired. If the fruit or other source of the flavouring is used in bulk, it is allowed to digest in the syrup for a period of 6 to 10 days, according to its character. The French are adepts in the manufacture of these preparations, and their use is more general with them than in this country, under such names as *absinthe* (flavoured with the tops of the *absinthium*), *groseille* (currant), *anisette* (anised), and numerous others. Extracts prepared in this manner are, however, largely used in England in confectionery and effervescing waters.

#### CORIANDEUR, OIL OF, *v.* OILS, ESSENTIAL.

**CORK.** The bark of *Quercus Suber*, a tree which grows in the south of France, Italy, and Spain, in North Africa and in the East. The bark is stripped from the tree in square sections, steeped in water, flattened under weights and dried before fires. It possesses a singular elasticity and toughness which make it available for stopping bottles and other similar purposes. Its lightness, moreover, leads to its use for life-belts and other purposes where exceptional buoyancy is required. The refuse of cork also, in the form of a kind of sawdust, is employed in the manufacture of a carpeting for floors.

Cork consists for the most part of *suberin*, a form of cellulose. *Suberin* may be obtained by exhausting the bark with solvents such as alcohol, ether, and sulphuric acid. Chevreul found also a fragrant substance *cerin*, a soft resin, a yellow and a red colouring matter, quercitannic acid, gallic acid, and a brown nitrogenous substance, salts of vegetable acids, calcium, and water. By treatment with nitric acid cork yields oxalic, suberic, and ceric acids.

*Anona palustris*, or cork-wood, growing in the West Indies, furnishes a soft wood from which corks are made.

**Cork, or Korker.** The name given in the Highlands of Scotland to *Lecanora tartarea*. It is made into a dye by bruising the lichen and macerating it in putrid urine for a space of several weeks, a quantity of salt being added. When the required crimson or purple colour is extracted, the material is brought to the consistency of a paste by the addition of lime or burnt shells, and is dried. As required for use the dried substance is powdered and boiled with alum. In Shetland both the dye and the lichen are called *Korkalett*.

#### CORNEOUS LEAD *v.* LEAD.

#### CORNISH CLAY *v.* CLAY.

#### CORNISH STONE *v.* CLAY.

#### CORNUTINE *v.* ERGOT OF RYE.

**CORUNDUM.** (*Corindon*, Fr.; *Korund*, Ger.) Native alumina; so called from its Hindu name *Kurand*, whence it is assumed that the mineral was originally brought to Europe from India. From its hardness, which is second only to that of

the diamond, it is sometimes known as *adamantine spar* (*Diamantspath*, Ger.). Most mineralogists, following Haüy, use the term corundum in an extended sense, so as to include the three minerals, adamantine spar, sapphire, and emery. Emery is an impure variety, never crystallised (*v. Emery*), but the other varieties crystallise in the rhombohedral system, usually in double six-sided pyramids and rhombohedra, with the basal plane. The cleavage is rhombohedral, and the mineral also splits, more or less interruptedly, parallel to the base, in consequence apparently of its laminated texture. The lustre is vitreous, and therefore different from that of diamond; some varieties exhibit a pearly lustre on the basal plane. It is optically uniaxial; double refraction negative,  $\omega = 1.769$ ,  $\epsilon = 1.750$ . The coloured varieties are markedly pleochroic. H. 9; sp.gr. 3.9-4.1. Infusible before the blowpipe; but with borax fuses, with difficulty, to a clear glass. Unattacked by acids. The fine powder strongly heated with cobalt solution gives the characteristic blue colour of alumina.

The dull-coloured and opaque varieties, to which the term corundum is sometimes restricted, occur chiefly in India, China, Siberia, and the United States. The mineral has been obtained for ages from the old crystalline and metamorphic rocks of Southern India, notably from the Salem District, Madras. Large deposits, of grey, red, or purple tints, occur near Singrauli, in S. Rewah, where it is systematically worked. The hardness of the mineral renders it difficult of extraction, and fire is often lighted against the face of the rock to aid in loosening fragments. The matrix of the Salem corundum was described by De Bournon as a distinct mineral under the name of *Indianite*, but it appears to be only a variety of the feldspar, anorthite. According to Newbold, the Indian corundum occurs in gneiss, mica-schist, or hornblende schist. (On Indian corundum *v. Man. Geol. Ind.* 3 [V. Ball], 1881, 421; and vol. 4 [F. R. Mallet], 1887, 46.)

In America large deposits of corundum occur in the older rocks of the Atlantic States, especially in N. Carolina and Georgia. In 1871 it was discovered by C. W. Jenks at Corundum Hill, Macon, N. Carolina, where the common varieties passed into brightly-coloured transparent forms, sufficiently fine in some cases to be cut as gem-stones, and interesting as affording the first instance of the occurrence of ruby and sapphire in their original matrix (*Q. J. G. S.* 30, 1874, 303).

This deposit, as well as that at Laurel Creek, Georgia, is now extensively worked by the Hampden Emery Company. The corundum at both localities occurs in association with peridotite and hornblende gneiss. Blocks weighing as much as 5,000 lbs. each have been extracted. The corundum is prepared for the market by a succession of crushings and washings, the dressed mineral being finally sifted so as to separate it into various grades of fineness, distinguished in trade by numbers; the finest and least valuable being known as 'flour.' The crushing is performed by means of stamps and rollers, but these require frequent repair in consequence of rapid wear due to the extreme hardness of the mineral. It is more difficult to

crush corundum than emery, in consequence of its superior hardness.

Corundum is largely used as an abrading agent. Taking the abrasive power of sapphire as 100, that of the American corundum varies from 90 to 97, while that of Naxos emery is only between 40 and 57. The abrasive power, or 'effective hardness,' is estimated by rubbing a weighed sample of the mineral on a piece of plate-glass; the glass is weighed before commencing the operation, and is re-weighed from time to time during the grinding, when its loss affords an estimate of the abrading power of the substance. Of late years corundum has been largely used in the form of 'corundum wheels,' which are prepared by incorporating the coarsely-crushed mineral with a medium that admits of being readily moulded. (On American corundum *v. T. M. Chatard in Bul. U. S. Geol. Surv.* No. 12, p. 45; and *Min. Res. U. S.* for 1883 and 1884, 714; and W. A. Raborg, *id.* for 1886, 585.)

The transparent varieties of corundum, when cut and polished, are highly valued as gem-stones. When blue it is termed *sapphire*, while the clear colourless stones often pass under the name of *white sapphire*. The red varieties are known as *ruby*, or as *oriental ruby*, the qualifying word being used to distinguish it from inferior stones, such as spinel, which are also termed 'ruby.' *Bakelite* is a turbid magenta-tinted corundum from Victoria. The other coloured corundums are generally known as 'oriental' stones; thus the yellow varieties, though sometimes called *yellow sapphire*, are usually termed *oriental topaz*; the purple stones are distinguished as *oriental amethyst*; and the green corundum, which is the rarest of all, is prized as *oriental emerald*. The following analyses of some typical forms of corundum were made by J. Lawrence Smith (*Am. S.* [2] 11, 1851, 54):

	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	HO <sub>2</sub>
Sapphire (India)	97.51	1.89	0.80	—	—
Ruby (India)	97.32	1.09	1.21	—	—
Corundum (India)	93.12	0.91	0.96	1.02	2.86
Corundum (Asia Minor)	92.39	1.67	2.05	1.12	1.60

It is believed that the ruby owes its colour to the presence of oxide of chromium. When strongly heated it becomes green, but regains its normal colour on cooling. The nature of the colouring matter of sapphire is not well understood; and though cobalt has been suggested its presence has not been proved, and it seems likely that some compound of chromium is here also the tinctorial agent. Certain sapphires become decolourised by heat. It is notable that in many sapphires the pigment is very locally distributed, so that the stone is parti-coloured.

Haidinger's dichroscope, which is frequently used to distinguish one gem-stone from another, may sometimes be usefully applied to the coloured corundums. In many sapphires the two images differ greatly in tint, one being dark blue while the other is pale bluish-green, or even yellowish; in other sapphires, however, the difference of tint is very slight. In dealing with highly pleochroic stones, the phenomenon may be observed with the unaided eye. Thus certain sapphires appear blue when viewed in the direction of the optic axis, or along the principal

axis of the prism, and green at right angles to this direction, or perpendicularly to the prismatic faces. In ruby the dichroism is not so marked as in sapphire. Viewed in the dichroscope one image may be deeper than the other; the red of the one inclining to violet; that of the other to yellow.

The ruby may be distinguished from all other red stones by its superior hardness. From spinel and rubellite it may be separated by its high specific gravity. If the dichroism can be detected, this character will distinguish it from either garnet or spinel, since these minerals crystallise in the cubic system and are consequently not pleochroic.

Coloured corundums frequently contain minute fluid cavities and microscopic crystals, which have been studied by H. C. Sorby and P. J. Butler (Pr. 17, 1869, 291). According to these observers the fluid cavities are more numerous in sapphire than in ruby; while the inclosed crystals are more abundant in ruby than in sapphire. The inclusions often give a milky and defective appearance to the stone, and when definitely orientated produce curious optical phenomena. It seems due partly to these lines of inclusions, and partly to a system of striations intersecting at  $60^\circ$ , that certain corundums, when cut with a convex surface, display by reflected light a luminous six-rayed star. This phenomenon is not uncommon in blue-grey opalescent sapphires, which are consequently known as *asterias* or *star-sapphires* (*Saphir astérié*; *Sternsapphir*). It is notable that the hardness of the sapphire slightly exceeds that of the ruby.

Sapphires are found as rolled crystals and pebbles in detrital deposits in Ceylon; and they occur with rubies in Upper Burma. A few years ago fine sapphires were discovered in the Zanskar range of the Himalaya mountains; and large deposits of dark-coloured stones have been found in the province of Batumbong in Siam. Near Helena, in Montana, U.S., rolled crystals of sapphire are found in placer mining. In Europe small sapphires occur in certain basaltic rocks, as in the Siebengebirge on the Rhine, and at Expailly, near Puy-en-Velay in France; but the European stones are worthless.

Sapphire is not uncommon in the gold-bearing drifts of N. S. Wales and Victoria, but the ruby is rare. The late A. M. Thomson, of Sydney, made the following analyses, cited by A. Liversidge in the Min. of N. S. W., 1888, 196:

	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$
Sapphire (Mudjee)	98.57	2.25	0.45	—
Ruby (Two-mile Flat)	97.90	1.39	0.63	0.52

Most, if not all, of the so-called 'Australian rubies' recently (1888) brought to this country are merely garnets. In like manner the garnets from the diamond mines at Kimberley pass in trade under the name of 'South African rubies.'

The true ruby is of much more limited distribution than the sapphire. It occurs but sparingly in the gem-bearing detritus of Ceylon, where sapphires are common. The chief ruby localities are at Mogok, Kyatpyen, and Kathley, in Upper Burma, where the rubies occur in detrital deposits and in a bed known locally as *pyon*. (R. Gordon, P. R. G. S., May 1888,

261). The Burmese ruby has been found by Barrington Brown in a matrix of calc-spar (r. Proc. Geol. Soc. 1888, 91; and G. S. Streeter, Journ. Soc. Arts, Feb. 22, 1889).

The artificial production of ruby has been effected at various times by Gaudin, Elsnér, Ebelmen, De Senarmont, Sainte-Claire Deville, and Caron and Debray; but it was not until the experiments of Fremy and Feil in 1877 that the substance was obtained on a commercial scale. By fusing a mixture of alumina and red lead in a fire-lay crucible, these experimentalists obtained a fused aluminate of lead, which was decomposed by the silica of the crucible with formation of silicate of lead, while free alumina crystallised out, on cooling, as white corundum. By the admixture of from 2 to 3 p.c. of potassium bichromate with the original materials, the resulting alumina separated in the form of ruby, while the association of a small proportion of oxide of cobalt with the potassium bichromate determined the production of sapphire (C. R. 85, 1877, 1029). More recently Fremy and A. Verneuil obtained fine artificial rubies by the reaction of barium fluoride at a red heat on amorphous alumina containing traces of potassium bichromate. The substance thus obtained possesses all the physical characteristics of natural rubies, and Des Cloizeaux has shown that they agree in crystalline form (C. R. 106, 1888, 565, 567).

The jewellery trade was much disturbed about 1886 by the appearance of large numbers of rubies, of fine colour, sold by a house in Geneva. Having excited suspicion, the stones were placed by the Paris 'Syndicat des Diamants' in the hands of M. Friedel for careful examination. He found them to agree with the natural ruby in all respects, except that they contained little spherical blebs, readily seen with a hand lens; whence he concluded that they had been formed by the fusion of a number of small rubies. Stones of small size are of comparatively little value, while a large ruby, of fine colour, always commands a very high price. Terreil and Verneuil have fused amorphous alumina in the oxyhydrogen blowpipe, and E. Jannettaz has examined the behaviour of this product when subjected to electric discharge in Crookes's exhausted tubes, and found it to agree with that of the Geneva rubies and the natural corundum by glowing with a vivid red light (Bl. S. F. M., 9, 1886, 321). G. F. Kunz, of New York, after an exhaustive examination of the Geneva rubies, has concluded that they were manufactured by Fremy and Feil's method, and not by fusion of small stones, since fusion lowers the density, Gaudin having shown that amorphous alumina after fusion in the OH blowpipe has a sp.gr. of only 3.45 (Min. Res. U. S. for 1886, 601; Trans. N. Y. Acad. Sc., October 4, 1886).

F. W. R.

#### CORUNTINE v. VEGETO-ALKALOIDS.

#### CORYDALINE v. VEGETO-ALKALOIDS.

**COTTON** is the soft hairy filament inclosing the seeds of various species of the plant *Gossypium*, nat. ord. *Malvaceae*. These plants are either herbaceous, shrubby, or arborescent in habit, and are said by Parlatore to embrace seven primary species. Other botanists limit the classification to four distinct species, the rest, in their



opinion, being merely varieties. The four enumerated are

1. *Gossypium barbadense*, herbaceous, embracing the long-stapled Sea Island cotton and a large part of the crop of Alabama, Mississippi, and other States of North America.

2. *G. peruvianum*, arboreous, indigenous to Peru, Brazil, and neighbouring countries of South America.

3. *G. herbaceum*, shrubby, indigenous to Asia, producing Indian or 'Surat' cotton.

4. *G. arboreum*, tree-like, China and India. The cotton-plant flourishes best in a warm damp climate, free from excessive rains and frost. Seed is sown from March to May, and picking takes place from August to October according to circumstances. The seeds of the plant are inclosed in a pod containing along with them fibrous locks of cotton-wool which on the bursting of the ripened pod is seen to be of a somewhat variable whiteness. The fibres are attached to the seeds and require to be torn from them by ginning after being picked from the bolls.

Crum described the fibre of mature cotton

as consisting of a hollow, shrivelled, irregularly-twisted cylinder thickest at the seed from which it originates and gradually diminishing as it recedes from it. Bowman, who has minutely examined and delineated the structure of the fibre, finds three main groups:

1. Those where no internal structure is apparent.

2. Where the structure seems to be simply tubular with a well-defined transparent cell-wall.

3. Where the structure is tubular and the interior of the cell filled with secondary deposits which almost entirely fill up the internal cavity, giving the fibre a dense, almost opaque appearance.

The same authority states that the fibres of wild cotton exhibit large and weak tubes when compared with cultivated specimens. The value of the cotton commercially is affected by even thickness of the fibre, but still more by the length of the staple. The following table shows the relative length and diameter of fibre in various descriptions of cotton:—

Length and Diameter of Cotton Fibres.

Place of growth	Description of cotton	Length of staple			Diameter of fibre		
		Inches			Inches		
		Min.	Max.	Mean	Min.	Max.	Mean
United States	New Orleans	0·88	1·16	1·02	·000580	·000970	·000775
Sea Island	Long stapled	1·41	1·80	1·61	·000460	·000820	·000640
South America	Brazilian	1·03	1·31	1·17	·000620	·000960	·000790
Egypt	Egyptian	1·31	1·52	1·41	·000590	·000720	·000655
India	Indigenous	0·77	1·02	0·89	·000649	·001040	·000844
	American seed	0·95	1·21	1·08	·000654	·000996	·000825
	Sea Island and						
	Egyptian seed	1·36	1·65	1·50	·000576	·000864	·000730

(From the Science of Modern Cotton Spinning, vol. 1, by Evan Leigh.)

Perfectly ripe cotton fibre consists of almost pure cellulose. There are, however, other substances usually present. Schunck treated yarn with boiling water containing soda-ash, and mixed the resulting dark-brown liquor with an excess of sulphuric acid which gave a precipitate of a light-brown colour. Two estimates gave—

Dhollerah 0·337 p.e.

Middling Orleans, 0·480 p.e.

Cotton contains from 2·3 to 6·9 p.e. of ash consisting chiefly of oxide of iron, alumina, and aluminium silicate, the remainder being calcium sulphate and sodium sulphate. The other substances consisted of—

1. *Cotton-wax*, a substance closely resembling vegetable waxes such as cerosine prepared from the leaves of the sugar-cane, and the wax from the leaves of the Carumba palm (*Corypha cerifera*). It is insoluble in water, but soluble in alcohol and ether; it fuses at 86°C., and solidifies again at 80° to 82°C. Pure cotton-wax is insoluble in caustic alkalis; it contains C 80·3, H 14·4, O 5·3.

2. Fatty acid, similar to margaric acid or a mixture of stearic and palmitic acids, fusing at 55·5°C. and solidifying again at 50·5°C., and of the composition, C 75·5, H 13·0, O 11·5.

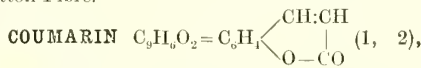
3. Colouring matter A, easily soluble in alcohol, containing from 5·22 to 8·03 p.e. nitrogen; one specimen gave C 58·48, H 5·80, N 5·31, O 30·41.

4. Colouring matter B, scarcely soluble in alcohol:—C 57·77, H 6·05, N 8·74, O 27·44.

5. Pectic acid.

6. Albuminous matter.

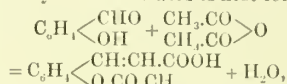
Mem. Lit. and Phil. Soc., Manchester; Schunck [3] 4; and Bowman's Structure of the Cotton Fibre.



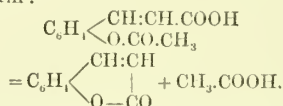
was obtained by Vogel (Gilb. Ann. 64, 161) in 1820, from the tonka bean (the seed of *Dipterix* (*Coumarouna*) *odorata*), or from the melilot (*Melilotus officinalis*), and from the woodruff (*Asperula odorata*), but was mistaken by him for benzoic acid. Guibort, however, showed that the crystalline odoriferous principle of the tonka bean was distinct from benzoic acid, and named it *coumarin*. It occurs in many other plants.

It was first obtained synthetically by Perkin by heating the sodium compound of salicylaldehyde with acetic anhydride (C. J. 1868, 53) or more simply by boiling together salicylaldehyde, acetic anhydride, and dry sodium acetate (C. J.

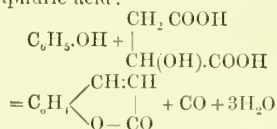
1887, 388; see also Tiemann and Herzfeld, B. 10, 284). Acetyl coumaric acid is first formed:



which then parts with acetic acid yielding coumarin:



Coumarin is also formed in small quantity by heating a mixture of phenol and malic acid with sulphuric acid:



(Von Pechmann, B. 17, 929).

It forms rhombic crystals melting at  $67^\circ$ ; boils at  $290-290.5^\circ$ ; has a pleasant, aromatic odour; is scarcely soluble in cold water, readily soluble in boiling water, very soluble in alcohol and ether.

It dissolves in caustic alkalis, and is reprecipitated on addition of acids. If, however, it is heated for some time with concentrated caustic alkali, or better, with sodium ethylate, a solution is formed from which acids precipitate coumaric acid  $\text{C}_6\text{H}_5 \left\langle \begin{array}{l} \text{CH:CH.COOH} \\ \text{OH} \end{array} \right\rangle$  (1, 2).

This compound can be reconverted into coumarin by heating it with acetic anhydride; but when heated alone it is decomposed, yielding phenol and other substances.

In Germany, woodruff (Ger. *Waldmeister*) is steeped in white wine, to which it imparts the pleasant aroma of coumarin (*Maiwein, Mai-trank*). Instead of woodruff, an alcoholic solution of coumarin is employed for the same purpose under the name of *Maiweinessenz*.

In larger doses coumarin is stated to have a narcotic action. F. R. J.

**COUPIER'S BLUE** v. INDULINES.

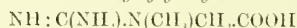
**COVELLITE.** Cupric sulphide v. COPPER.

**COWDIE GUM** v. RESINS.

**COW TREE WAX** v. WAX.

**CREAM OF TARTAR** v. TARTARIC ACID.

**CREATINE** Methyl-glycoeyamine



in the anhydrous state forms an opaque, white, solid, inodorous substance, possessing a somewhat bitter acid taste. Its monohydrate crystallises in clear prisms, losing their water of crystallisation at  $100^\circ\text{C}$ . Creatine is soluble in about 70 parts of water, but almost insoluble in absolute alcohol. Creatine is one of those constituents of meat soups and extracts which impart appetising taste and stimulating action to the heart and muscular centres. T. J. Mays has shown that creatine solutions as weak as 1:2,000 are capable of re-animating a frog's heart which has been fatigued, and finally arrested, by administration of sodium chloride. Kobert (C. Z. 1888, 1662), as the result of experiment, recommends this principle as of undoubted

value as an excitant of muscular action in the case of the heart, digestive organs, and general muscular system (S. C. 1, 8, 476).

**CREOSOTE** or **KREJSOTE** (from *κρέας*, contracted genitive of *κρέας*, meat, and *σώζω*, I save or preserve). Wood tar, and coal tar, when subjected to distillation yield fractions technically known as 'creosote,' both of which, the latter more especially, find extensive and important uses in the industrial arts.

Reichenbach, in the year 1832, applied the term 'kresote' to a substance derived from wood tar, and which had been found to possess powerful antiseptic properties; shortly afterwards Runge discovered carboic acid in coal tar, and the two products were for a considerable time regarded as identical; similar compounds, however, have since been procured from other sources, and in view of this fact, and in order to avoid confusion, it has been suggested that the term 'creosote' should be applied in a generic sense as referring to the phenols and phenoloid bodies derived indifferently from wood tar, coal tar, blast-furnace tar, and shale oil.

**Wood-tar creosote.** The tar derived from the distillation of beechwood, when subjected to further distillation, yields certain fractions that are heavier than water, and which after agitation with solution of caustic soda, and separation from insoluble oils, are boiled with free access of air in order to oxidise various impurities present; the alkaline solution thus obtained is decomposed with dilute sulphuric acid, the crude creosote which separates is again submitted to a similar alkaline and acid treatment, and the product finally distilled, reserving the fraction passing over between  $200^\circ$  and  $220^\circ\text{C}$ . This represents the ordinary 'wood-tar creosote' of commerce. It is a complex mixture of phenoloid compounds, the proportions of which are materially influenced by the method originally followed in distilling the beechwood from which it was obtained.

Wood-tar creosote when freshly prepared is a colourless, transparent liquid of an oily consistency, and which retains its fluidity at a very low temperature; its sp.gr. varies from 1.037 to 1.087; it boils at  $205-225^\circ\text{C}$ , and dissolves in about 200 parts of water; its odour is strong and penetrating, resembling that of wood smoke, or rather of smoked meat; it refracts light powerfully, and burns with a very sooty flame. Wood-tar creosote is powerfully antiseptic, but its power of coagulating albumen has been denied; nevertheless, it preserves animal substances as effectively as carboic acid. It is less caustic than carboic acid and is not poisonous.

Wood-tar creosote may be regarded as consisting of a mixture of compounds included in several homogeneous series, chiefly of acid methylic ethers of catechol, and the presence of the following bodies has been established:—

Name	Formula	Boiling point
1. Monohydric phenols:		
Phenol, carboic acid . . .	$\text{C}_6\text{H}_5\text{OH}$	182°
Paracresol, cresylic acid . . .	$\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$	203°
Xylenol, or phloral . . .	$\text{C}_6\text{H}_3(\text{CH}_3)_2\text{OH}$	220°

2. *Methylic ethers of dihydric phenols:*

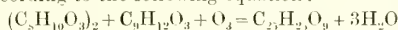
Name	Formula	Boiling point
Guaiacol, or methyl catecholate	$C_6H_4 \left\{ \begin{array}{l} OCH_3 \\ OH \end{array} \right\}$	200°
Creosol, or methyl methyl-catecholate	$C_6H_3(CH_3) \left\{ \begin{array}{l} OCH_3 \\ OH \end{array} \right\}$	219°
Homocresol, or dimethyl-guaiacol	$C_6H_2(CH_3)_2 \left\{ \begin{array}{l} OCH_3 \\ OH \end{array} \right\}$	230°
Cærulignol, or propyl-guaiacol	$C_6H_3(C_3H_7) \left\{ \begin{array}{l} OCH_3 \\ OH \end{array} \right\}$	241°

3. *Methylic ethers, or trihydric phenols:*

Dimethyl pyrogallate	$C_6H_3 \left\{ \begin{array}{l} OCH_3 \\ OCH_3 \\ OH \end{array} \right\}$	253°
Dimethyl-methyl-pyrogallate	$C_6H_2(CH_3) \left\{ \begin{array}{l} OCH_3 \\ OCH_3 \\ OH \end{array} \right\}$	265°
Dimethyl-propyl-pyrogallate (picamar)	$C_6H_2(C_3H_7) \left\{ \begin{array}{l} OCH_3 \\ OCH_3 \\ OH \end{array} \right\}$	285°
Methyl-propyl-pyrogallate	$C_6H_2(C_3H_7) \left\{ \begin{array}{l} OCH_3 \\ OH \\ OH \end{array} \right\}$	290°

Of these compounds phenol is present in extremely small quantity, paracresol in larger, and phloral in notable proportion, but the two principal constituents of creosote are guaiacol and creosol, although not equally present in all varieties; guaiacol, according to Allen, predominates in Rhenish creosote, whilst with Morson's creosote from 'Stockholm tar,' creosol is the chief constituent. Homocresol, and cærulignol are present in small quantity only, but, according to Grätzel, the latter body possesses such energetic and astringent qualities that a single drop placed on the tongue causes bleeding; purified creosote should therefore be absolutely free from this compound which may be detected by the blue colouration produced by barium hydroxide.

The less valuable portions of wood-tar creosote have been found by A. W. Hofmann to contain the methylic ethers of pyrogallol and its homologues; these bodies are of interest from the remarkable colouring matters (originally discovered by Runge) which may be derived from them by oxidation; thus, if the sodium derivate of dimethyl pyrogallate be mixed with the sodium derivate of dimethyl methyl-pyrogallate and excess of sodium hydrate, and heated in the air, a substance called eupittonic acid is formed according to the following equation:—



Eupittonic acid has the constitution of a hexamethoxyl aurin,  $C_{16}H_{10}(OCH_3)_6O_9$ . Reichenbach's 'pittacal,' called by Wichelhaus 'eupittone,' was a salt of eupittonic acid. Wood-tar creosote has been met with adulterated to a considerable extent with crude carbolic and cresylic acids, and from the fact that the reactions of these substances closely resemble those of wood creosote, the distinction between the two, especially when in admixture, is attended with some difficulty. Genuine beechwood tar is soluble in solutions of caustic alkalis, and forms a crystalline compound with potassium hydrate, but not with soda; on the other hand, it is practically insoluble in strong ammonia.

An alcoholic solution should give no colourations whatever (blue or red) with baryta water; such colouring indicates the presence of cærulignol and other impurities.

Wood-tar creosote is sharply distinguished from the coal-tar acids by its insolubility in absolute glycerine; it is also distinguished from the coal-tar acids by its reaction with an ethereal solution of nitrocellulose; shaken with half its volume of collodion, B. P., Calvert's No. 5 carbolic acid coagulates the gun-cotton. Morson's creosote does not precipitate the nitrocellulose from collodion, but mixes perfectly with the ethereal solution; when a mixture of equal volumes of Morson's creosote and Calvert's No. 5 acid is thus treated with the collodion, the precipitation of nitrocellulose is very marked.

**Coal-tar creosote, Heavy oils, Dead oils.**

This substance, both as regards the magnitude of its production, and the extensive uses to which it is applied, occupies a position of considerable interest and importance. As a distillate derived from coal-tar it represents the fraction passing over between 204° C. and 404° C.

As far as can be gathered from trustworthy statistics the annual production of creosote in the United Kingdom amounts to about 29,900,000 gallons, which is now more or less disposed of in the creosoting of timber, softening of hard pitch, as liquid fuel, for lighting, burning for lamp-black, as an antiseptic, and as a cattle wash for the destruction of animal parasites. Coal-tar creosote differs considerably in appearance and character; that known as 'London make' exhibits a deep-greenish shade, and is more or less fluorescent; it is highly charged with naphthalene, and is not unfrequently viscid or semi-solid at ordinary temperatures. 'Midland or country' creosote shows less fluorescence and is both thinner and more volatile. The 'Scotch' creosotes derived from canal coal are still thinner and proportionately more volatile, and not unfrequently lighter than water; creosote oil from London coal-tar is always heavier than water, the sp.gr. of the portions last distilling reaching as high as 1.10, but the mean of the mixture may be taken at 1.065, while for country make it seldom exceeds 1.05. Coal-tar creosote possesses a strong unpleasant odour, highly characteristic of the fluid, and which readily distinguishes it from all others.

Any attempt to determine the absolute composition of coal-tar creosote is attended with much difficulty, but the following substances are known to be present: Naphthalene, phenanthrene, anthracene, pyrene, chrysene, carbazole, benzerethrene, and other solid hydrocarbons accompanying the distillation of the tar.

Various phenoloid bodies are also present consisting of carbolic and cresylic acids, with higher phenols concerning which little is really known: Basic substances consisting of the heavier members of the pyridine series, cryptidine-quinoline—and acridine are also present together with the so-called indifferent oils, fluid at ordinary temperatures, and about which still less is known. Carbolic and cresylic acid vary greatly in the proportion found; for 'London creosote' the average yield of total tar acids may be stated at 4 to 7 p.c.; while for 'country make' the quantity is often considerably higher, but



the bulk of the pyridine or basic bodies contained in the coal tar passes over in distillation of the lighter oils.

*Employment of creosote oil for preserving timber (creosoting).—*The preservation of timber by antiseptic treatment, more especially when employed for railway sleepers, telegraph poles, piles for harbours, marine, and such like purposes, has become an established industry, the importance of which is now widely recognised both in England and abroad. By far the larger portion of the oils distilled from gas tar is consumed and utilised in the creosoting of timber, and to an extent that has from the earliest period of the operation closely connected it with the process of tar distilling; indeed, there is little difficulty in tracing the earlier development of 'tar distilling' to the demands for such oils consequent upon the introduction of Bethell's process in the year 1838.

The preservation of timber by antiseptic methods has engaged the attention of many chemists and engineers; and in the treatises of Adolf Mayer, *Chemische Technologie des Holzes* (Braunschweig, 1872), Buresks *Der Schutz des Holzes* (2nd ed., Dresden, 1880), and Heinzerling's *Die Conservirung des Holzes* (Halle, 1885) a vast amount of detail has been furnished. From Mr. Boulton's treatise (*The Antiseptic Treatment of Timber*, Proc. Inst. Civ. Eng. 1883-84, 78, 4) we gather that as far back as the year 1838 four important systems of preserving timber were before the public, viz.: (1) Corrosive sublimate, known since 1705, and again introduced by J. H. Kyan; (2) sulphate of copper, known since 1767, principally introduced by Margary and Boucherie; (3) chloride of zinc, known since 1815, patented again by Sir W. Burnett; and lastly, (4) heavy oil of tar, afterwards called creosote oil, by John Bethell; the latter process exceeds the others in utility, and in England has replaced them entirely.

The apparatus generally used for the creosoting of timber was originally suggested by Brant, director of the Paris Mint in 1831, modified by J. Bethell, and finally considerably improved by H. P. Burt. Practically it consists of a strong, horizontal, wrought-iron cylinder 6 to 7 feet in diameter, and 30 to 60 feet long. The timber to be impregnated is packed on iron trucks which are run upon rails into the cylinder, the opening to which is finally closed by an air-tight cover swung in front of the cylinder. Attached to this cylinder is a suitable air-pump, by means of which the contained air is withdrawn until the air-gauges indicate an exhaustion equal to the  $\frac{2}{3}$  or  $\frac{1}{2}$  of an atmosphere; creosote oil heated to a temperature of about 50° is then admitted, and, in consequence of the partial vacuum and removal of air from the pores of the wood, penetrates to some extent into its mass; when the oil ceases to be imbibed, a force-pump is brought into play, and more creosote is injected into the cylinder till a pressure of 8 to 10 atmospheres has been obtained. This operation is maintained for several hours, during which time fir timber, under treatment, will take up from 40 to 60 gallons per load of 50 cubic feet. One of the chief difficulties encountered in carrying out the process thus described is the presence of moisture in the timber; as freshly cut, or as removed from the

'timber ponds,' it is not in a condition suitable for creosoting, and requires several months stacking as a preliminary to the operation. Numerous attempts have been made to obviate the loss of time consequent upon this method of drying, but all endeavours to employ artificial heat have failed. It has been found that the application of such heat at a temperature sufficient to drive off rapidly the contained moisture invariably injures the woody tissue.

Attempts have also been made to inject creosote oils in the state of vapour (Lukin, 1812; Franz Moll, 1836; and Bethell, 1861), but the heat of the injected vapour seriously impaired the value of the timber.

Blythe, of Bordeaux (G. P. 10, 423), patented a method of injecting superheated steam into creosote oil, and allowing the mixed vapours of steam and oil to act upon the timber. This process has been tried on a large scale, especially in France; but the difficulties attending the injection of creosote into timber in the form of vapour are as yet insuperable. By no method can creosote be volatilised and injected under pressure, except at a temperature which will injure the timber. The boiling-point of creosote ranges from 204.5°C. to 401.5°C., whereas it is dangerous from an engineering point of view to subject timber to a greater heat than about 121°C. In practice, therefore, the temperature necessary to volatilise the creosote is not reached, whence it follows that only the vapour of water can be driven into the creosote; hence, wherever this process is still used, it is supplemented by the injection of creosote in the ordinary fluid condition (*v. Mittheilungen des Architekten- und Ingenieur-Vereines im königreiche Böhmen, and Minutes of Proceedings of Civil Engineers*, 78, part 4, Session 1883-4).

One of the most effective methods of dealing with damp timber is that patented by S. B. Boulton (B. P. No. 1854 of 1879), by which the timber may be introduced into the creosoting cylinder quite wet; it may be briefly described as follows:

The timber to be creosoted is placed in a cylindrical vessel provided with a somewhat high dome, and from which an exit pipe passes on-wards to a condensing worm and receiving tank in direct connection with an air-pump. After the air has been withdrawn in the usual manner, the creosote is introduced at a temperature of a little above 100°C. and in quantity so that the dome shall at all times be empty. The exhausting process is continued until the whole of the moisture contained in the pores of the wood has been vapourised by the heat of the creosote oils, and has been drawn away by the air-pumps connected therewith.

As the temperature employed is considerably below the boiling-point of creosote, this liquid is not converted into vapour, and with charges of wet sleepers the patentee has succeeded in withdrawing water equal to 50 gallons per load of timber, and replacing this water with an equal volume of creosote by the action of the air-pump alone. The process thus described involves a trifling additional cost and a few more hours for the treatment of very wet timber, but the expenditure in time and money is not so great as

would be required by storing the wood before creosoting.

With respect to the suitability of a given creosote for the purpose of creosoting, it has been held, on the one hand, that those products known as 'country make,' rich in tar acids, possessed the highest value. On the other hand, it has been argued that the quantity of tar acids present is no measure of its applicability to timber preserving, and that the tar acids themselves, *i.e.* carboic and cresylic acid, although highly useful as sanitary antiseptics, are of no permanent value in the preservation of timber, owing to their volatility and their solubility in water, and that they do not enter into permanent combination either with albumen or woody fibre. It has been found that the heavier basic bodies of the pyridine series, with acridine, and even naphthalene, play an important part in determining the character of creosote as an antiseptic.

Mr. Boulton is of opinion that the tar bases (pyridine series), and especially acridine, are also very useful as antiseptics in creosote, and his view has been fully borne out by trials made by Mr. Greville Williams (*Journal Gas Lighting*, June 5, 1883). It is now generally held that the 'creosote employed for preserving timber should be of a heavy rather than of a light description, *i.e.* that it should contain oils which are given off at a high temperature, together with other matters that become solid within the timber after the creosote has been allowed to cool to a normal temperature.'<sup>1</sup>

In accordance with these views a form of specification for creosote was prepared by Dr. Tidy, which has since become very generally recognised in the selection of that substance.

It stipulates:

1. That the creosote shall be completely liquid at a temperature of 100°F.; no deposition afterwards taking place until the oil registers a temperature of 95°F.

2. That the creosote shall contain at least 25 p.c. of constituents that do not distil over at a temperature of 600°F.

3. That the creosote shall yield a total of 8 p.c. of tar acids.

The process for determining the quantity of tar acids is as follows:—

1. 100 c.c. of the well-mixed creosote are distilled at a temperature of 600°F., until no further distillate comes over. The distillate is mixed and well shaken in a stoppered flask, with 30 c.c. of a solution of caustic soda, having a sp.gr. of 1.200. The mixture is then heated, the stopper replaced in the flask, and the hot mixture again vigorously shaken for at least a minute.

The contents of the flask are now to be poured into a separating funnel, and the soda solution drawn off. The creosote is to be heated a second and a third time in a similar manner with the caustic soda solutions, except that only 20 c.c. of the soda solution are used for the second and third extraction, instead of 30 c.c., as in the first extraction.

2. The three soda solutions are now to be

mixed together. When cold, any particles of creosote are to be removed by a separating funnel. The solution is then to be thoroughly boiled, in order to expel the last traces of creosote present in the solution. When cold dilute sulphuric acid (1 of acid to 3 of water) is to be added (about 35 c.c. will be required) until the solution becomes acid to litmus. The whole is then to be poured into a separating funnel, and allowed to stand until perfectly cold, and the tar acids separated.

3. The tar acids are now to be dissolved in 20 c.c. of the caustic soda solutions (sp.gr. 1.200) and 10 c.c. of water. The mixture is then to be boiled and filtered through a funnel fitted with a plug of asbestos. The asbestos plug is to be washed with not more than 5 c.c. of boiling water. The solution is to be allowed to cool perfectly in a 100 c.c. measure. It is then to be rendered slightly acid with dilute sulphuric acid (1 to 3; 10 c.c. will probably be found sufficient for this purpose). The whole is again allowed to stand for 2 hours until perfectly cold, when the percentage of the tar acids is to be read off.

*Process to be adopted in estimating the quantity of distillate.*—The operation is to be conducted in a retort (fitted with a thermometer) immersed in an oil or hot-air bath. The heat at first to be low, and the temperature gradually raised to 600°F., and continued until no further matters distil over.

Sir Frederick Abel has also devised a specification and test, known as that of January 2, 1881. It agrees very closely with that of Dr. Tidy.

*Employment of creosote oils for softening pitch (v. Prent).*

*Employment of creosote oils for lighting.*—

Creosote oil has long been employed as a source of light in the construction of harbours and out-door work, where smoke was of little consequence or inconvenience; but when it is wished to burn this oil to the greatest advantage, and with the least possible amount of smoke and soot, it becomes necessary to employ lamps so constructed that a jet of air or of steam, more or less superheated, may be introduced in such a manner as to ensure more perfect combustion.

Hartmann and Lucke (Ger. Patent, No. 9,195, August 9, 1879) construct a lamp specially intended for the consumption of creosote oils, in which the oil is automatically supplied to a dish-shaped receptacle, over which is placed a funnel-shaped cylinder; in the centre of the dish or receptacle receiving the oil from its attached reservoir is placed a conical tube, reaching a little above the surface of the oil, and through which a jet of superheated or dry steam may be driven. In using the lamp, the dish or receptacle referred to is allowed to fill with oil; it is then ignited at its surface, the funnel-shaped cylinder placed over it, and steam cautiously admitted through the conical tube. It will readily be seen that the arrangement closely resembles the old 'Herapath blowpipe,' with the difference that steam is forced through a body of combustible fluid, issuing just above its surface, in place of air forced through a body or envelope of combustible gas, and issuing at a point or position that may be called its surface. The oil thus burns without wick or chimney,

<sup>1</sup> It may be stated that attempts have recently been made in America to employ the thinner creosotes for timber preserving, but they were found to be less efficacious than the heavier oils.

and affords a light of 180 standard candles, with an hourly consumption of a little over 2 lbs. of creosote.

An apparatus for a similar purpose has been patented by Lyle and Hannay, under the name of the 'Lucigen.' It consists of an oil tank or reservoir, fitted with a special burner at the top of a tube, which may be extended to any length; into this reservoir compressed air is introduced by an india-rubber pipe, so attached as to make the 'Lucigen' portable. On the compressed air being admitted into the oil tank or receptacle, it forces the oil up through an internal tube, and, escaping at the same time with the oil in the burner, produces a spray which is set on fire. A light of about 2,000 candle-power is given by the 'Lucigen.' The flame is large, the light well diffused, and the eyes are not dazzled by it. There is little or no smoke from the flame, and the lamp burns equally well under heavy rain or spray; it requires no lantern, and has no parts which can be damaged by rough usage.

In the 'Doty' light, pressure is brought to bear on the surface of the oil or creosote by means of an air pump, whereby the oil is forced through a coil surrounding the lower portion of the flame, and becomes distilled into gas.

Creosote oil has also been employed for the purpose of illuminating and heating, by direct conversion into permanent gas. A ton of creosote is capable of yielding 13,300 cubic feet of gas, with an illuminating power of 14 candles; a yield of 29,300 cubic feet may be obtained, but of 8½ candle-power only; the chief drawback to this method of utilisation is in the high temperature necessary to decompose the oils, and which results in the production of low candle-power gases.

*Employment of creosote oil as fuel.*—Creosote oil is extensively employed as a fuel, both for marine and stationary purposes, and, from theoretical considerations, would appear to be eminently adapted to the purpose, 1 lb. of coal-tar creosote, when effectively burnt, being capable of evaporating 11·24 lbs. of water, a result considerably in excess of that obtained from coal or coke.

Various methods have been devised for burning the oil to the greatest advantage; these may be briefly summarised under the following heads:—

1. Injection into the furnace by means of compressed air, with 'atomising' apparatus.
2. Injection into the furnace by means of steam, with 'atomising' apparatus.
3. Feeding into the furnace by simple gravitation, alone or in combination with coke.

G. F. Dexter (Jour. Gas Lighting, June 29, 1886, pp. 1242-1244), in a table showing the relative calorific values of certain coal-tar distillates, refers to creosote, or heavy oils, as under:—

Average formula $C_{11}H_{10}$	
Boiling-point, $240^{\circ}$ to $270^{\circ}$ and upwards.	
Proportionate weight of constituents:—	
Carbon . . . . .	0·93913
Hydrogen . . . . .	0·06387
Calorific value:—	
Carbon units . . . . .	497
Hydrogen units . . . . .	210

*Employment of creosote oil as an antiseptic and for the purposes of a cattle wash and sheep dip.*—Creosote oil as a fluid, and apart from timber preserving, finds but little application as an antiseptic, chiefly owing to its disagreeable smell, and insolubility in and immiscibility with water.

The latter drawback was removed by the process of Mr. Little (Patent No. 198, January 18, 1876), by which coal-tar creosote was rendered completely miscible with water. According to this patent, a mixture is formed, consisting of coal-tar creosote, 59·1; rosin oil, 29·6; oleate of potash, 5·9 (containing 0·59 potash), and 5·4 of a 10 p.e. solution of caustic soda (containing 0·54 soda) = 100·00.

These substances are blended in a special manner set forth in the patent, and yield a fluid scarcely differing in appearance from ordinary creosote, but differing greatly in character—that is to say, it may be added to water in considerable quantity, forming a clear milky emulsion, without any separation of creosote or oily particles, and which remains permanent on standing. This patent is worked by the firm of Morris, Little & Son, of Doncaster, and is the product sold under the name of 'soluble phenyle.' Mixed with water in the proportion of 1 to 100, or even stronger, it is extensively used as a sheep dip for the destruction of tick and other organisms of parasitic origin.

Further patents having a similar object were afterwards secured by J. and W. Jeyes (No. 4,636, December 7, 1877, and No. 5,249, December 23, 1878), by which the use of rosin oil and soft soap was obviated.

Samples analysed by the writer from material made under these patents, and supplied as sheep dips, gave the following figures:

Creosote . . . . .	60·4
Rosin . . . . .	29·6
Caustic soda . . . . .	2·4
Water . . . . .	7·6
	100·00

These substances, blended in the manner set forth in the patents referred to, furnish a fluid equally capable of mixing or emulsifying most perfectly with water, which is in extensive use under the name of 'Jeyes' disinfectant.'

Similar preparations are also in the market under the name of 'carbulated creosote.'

The consumption of these fluids (exported to America, Australia, and other great cattle stations) is very considerable. Creosote oils to the extent of about 100,000 gallons per annum are consumed in the preparation of these 'dips.' The preparations thus briefly described are non-poisonous, which gives them considerable advantage over many in use containing arsenic and metallic preparations.

The best method of ascertaining the complete solubility or 'miscibility' of these preparations in water consists in filling a dial glass six inches in diameter about three-fourths full of distilled water, and placing one drop of the prepared creosote on its inner surface in close proximity to that of the water. As the drop runs down and meets the water it is rapidly taken up, *playing over its surface with a rapid motion*, rendering it milky or opaque, and so on till



complete disappearance. Any residue of creosote or of the preparations left adherent to the glass betrays an imperfectly made material.

*Creosotes from other sources (blast furnace, coke oven, and shale oil).*—Several creosotes of this character have been studied by Watson Smith and A. H. Allen; they have been found to differ materially from those derived from coal and wood tar, occupying an intermediate position. The waste gases issuing from blast furnaces deposit a considerable quantity of tar yielding a creosote greatly resembling that furnished by gas tar; it differs, however, in the character of the phenoloids obtained from it; one of these bodies extracted by Watson Smith contained only 1.33 p.c. of real phenol, boiling at 182°C., whereas the tar acids from Lancashire tars yield 65 p.c. of crystallisable carbolic acid. The fractions passing over between 210° and 230°C. contain phloral and cresol, and those following at a higher temperature—viz. 360°—furnish compounds allied to the eupittonic acid obtained from wood tar.

A similar feature characterises the products furnished by coke oven and other allied tars. All yield phenoloids that approximate more closely to those from wood tar; but creosote derived from shale oil, although presenting a close resemblance to that from wood tar, differs in several respects; cresol appears to be entirely absent; on the other hand, phloral is present, as also a cymenol boiling at 237°C. The pyrogallic ethers boiling respectively at 253°, 265°, and 285°C., found by Hofmann in wood creosote, have also been separated from shale creosote. 'Blast furnace creosote oil' is now produced in vast quantities in Scotland, and the question of application has received a considerable amount of attention. To a certain extent it has been employed for creosoting timber, in producing the 'lucigen' light, and as a liquid fuel. It furnishes from 20 to 35 p.c. of phenoloid substances soluble in caustic soda, as against 4 to 7 p.c. in London coal tar creosote, and about 16 p.c. for Midland or country make. Allen and Angus, who have closely studied these bodies, have recently secured by patent their use as an antiseptic under the name of 'neosite,' a word signifying 'new preserver' (E. P. 11,689, August 29, 1887). Experiments have shown that the substance compares favourably with carbolic acid, while its caustic properties (when applied to the skin) are very much less marked. When freshly prepared the fluid is almost colourless, and bears the greatest resemblance to wood tar creosote.

*Bibliography.*—Lunge's Coal Tar and Ammonia, 2nd edit. 1887; Boulton on the Antiseptic Treatment of Timber (Proceedings of the Institution of Civil Engineers, 78, session 1883-84, part 4); Allen's Commercial Organic Analysis, 2nd edit. 1886. B. N.

**CRESOL**  $C_6H_4(CH_3)OH$ . The three isomeric cresols exist in coal tar (Williamson and Fairlie, A. 92, 319; Ihle, J. pr. [2] 11, 112; Tiemann and Schotten, B. 11, 767, 783) in about the following proportions: Orthocresol 35 p.c., metacresol 40 p.c., and paracresol 25 p.c. (Schulze, B. 20, 110).

The cresols can be separated from the oily, non-crystallisable mother liquors obtained in

the purification of crude phenol by fractionation and crystallisation, by dissolving them in soda-ley, freeing the solution from naphthalene or other hydrocarbons by a current of steam, and then fractionally precipitating with sulphuric acid. The first fractions, owing to the greater acidity of phenol, contain chiefly cresols, and are further purified by distillation (Miller, Z. 1865, 270). The isomeric cresols, however, cannot be obtained pure from this product, and must be prepared synthetically.

*Preparation of ortho- and para-cresol.* Pure ortho- and para-cresol can be obtained by fusing the potassium salts of the corresponding toluene-sulphonic acids with alkali (Engelhardt and Latschinow, Z. 1869, 620), or by diazotising the corresponding toluidines. For this purpose the toluidine (15 parts) is dissolved in sulphuric acid of sp.gr. = 1.8 (15 parts) diluted with 500 parts of water, treated with an aqueous solution of potassium nitrite (12 parts), and the product gradually heated with steam. The resulting cresol is then distilled with steam, the distillate treated with soda-ley, then with sulphuric acid, and the liberated cresol extracted with ether and finally distilled in a current of carbon dioxide (T. & S.; I.).

*Orthocresol* can also be obtained from carvacrol by treatment with phosphorus pentoxide (Kekulé, B. 7, 1006). It is crystalline, melts at 30° (T. & S.; I.), at 31-31.5° (K.), boils at 188° (T. & S.), and on fusion with caustic potash is converted into salicylic acid. When nitrated it yields dinitro-orthocresol (m.p. = 85-8°) (Nölting and Salis, B. 14, 987).

*Metacresol* is prepared by heating thymol (100 parts) with half its weight of phosphorus pentoxide for 10-12 hours until propylene ceases to be evolved, adding the product to 115-120 parts of fused alkali, and further heating the fused mixture for 5-10 minutes to decompose the cresyl phosphate formed. The melt is then dissolved in water, treated with ether to remove any undecomposed cresyl phosphate and other impurities, then acidified with hydrochloric acid, and the separated metacresol extracted with ether, and finally distilled in a current of carbon dioxide (E. & L., T. & S.). It is ordinarily a liquid, but has been obtained in crystals melting at 3-4° (Städel, B. 18, 3443); it boils at 211° (Oppenheim & Pfaff, B. 8, 886). Its aqueous solution is coloured blue by ferric chloride. When fused with caustic potash it is converted into metahydroxybenzoic acid, and on nitration it yields a trinitro-derivative (Nölting & Salis, B. 11, 987; 15, 1858).

*Paracresol* crystallises in prisms, melts at 36° (Barth, A. 151, 358), 36-37° (T. & S.), and boils at 198° (I.), at 198-199° (T. & S.). Its aqueous solution gives a blue colour with ferric chloride. When fused with caustic potash it is converted into parahydroxybenzoic acid, and on nitration it yields a dinitro-derivative (m.p. = 82.5°) (Richter, A. 230, 313; Nölting & Salis, l.c.).

A mixture of nitro-derivatives, obtained by sulphonating coal tar cresol and nitrating the sodium salt of the resulting cresolsulphonic acid with nitric acid of sp.gr. = 1.2, has been employed, under the names 'Victoria yellow,' 'saffron surrogate' (*q. v.*), as a dye for wool and

silk, and, although poisonous (compare Weyl, B. 20, 2835; 21, 512), is occasionally used as a colouring matter for butter, cheese, &c.

**CRESOL RED** *v.* Azo-COLOURING MATTERS.

**CRESYLIC ACID.** The non-crystallisable, higher boiling portion of the phenols obtained in the purification of phenol (*q. v.*) is, after re-distillation, known commercially as cresylic acid or liquid carbolic acid. It is a colourless, oily liquid, consisting chiefly<sup>1</sup> of the three isomeric cresols, and has a sp.gr. = 1.044. It does not solidify at  $-80^{\circ}$ , is much less soluble in water and alkalis than phenol, and also boils at a higher temperature (about  $185-203^{\circ}$ ). Its antiseptic properties are more marked than those of phenol (Lunge, Coal Tar and Ammonia, ed. 1887, 142).

**CRITH.** The weight of a litre of hydrogen at  $0^{\circ}\text{C}$ . and 760 mm. pressure—viz. 0.0396 grams.

**CROCEÏN** *v.* Azo-COLOURING MATTERS.

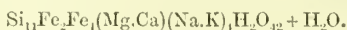
**CROCEÏN, BRILLIANT,** *v.* Azo-COLOURING MATTERS.

**CROCEÏN ORANGE** *v.* Azo-COLOURING MATTERS.

**CROCEÏN SCARLET** *v.* Azo-COLOURING MATTERS.

**CROCEÏN YELLOW** *v.* NAPHTHALENE.

**CROCIDOLITE.** (*Krokodyolith*, Ger.) In 1831 Hausmann gave this name to a fibrous mineral from South Africa, which was shown by Stromeyer to be a hydrated silicate of iron, sodium, and magnesium (Götting. gelehr. Anz. 1831, 1, 585; P. A. 23, 153). The name (from *κροκίς*, 'wool') alluded to the asbestiform texture of the mineral. A similar substance, brought from near the Orange River by the African traveller Lichtenstein, had been examined by Klaproth, who described it as early as 1815 under the name of *Blaueisenstein* (Beitr. 6, 1815, 237). In some varieties the fibres are blue, in others brown. The original crocidolite has been generally regarded by modern mineralogists as closely related to *arfvedsonite*, a soda-bearing mineral of the hornblende group (Rammelsberg, Min. Ch. 2 Auf. 1, 1875, 408). An analysis by Renard and Klement gave  $\text{SiO}_2$ , 51.89;  $\text{Fe}_2\text{O}_3$ , 19.22;  $\text{FeO}$ , 17.53;  $\text{CaO}$ , 0.40;  $\text{MgO}$ , 2.43;  $\text{Na}_2\text{O}$ , 0.15;  $\text{K}_2\text{O}$ , 0.15;  $\text{H}_2\text{O}$ , 2.36 (Bull. Ac. Roy. Belg. s. 3, t. 8, 1881). Assuming that part only of the water is basic, the authors deduce for crocidolite the following formula:



Klaproth was aware of the existence of another South African mineral occurring with the crocidolite, but regarded by him as a fibrous form of quartz. This *Faserquarz*, which was afterwards confounded with the true crocidolite, is the mineral which has of late years become fashionable as an ornamental stone. It is a hard fibrous mineral, generally of rich brown colour, but in some cases blue or bluish-green and occasionally white. Formerly it was exceedingly scarce, and known only in mineralogical cabinets, but since the development of the diamond fields of Griqualand West immense quantities have been brought to Europe. Like most

fibrous minerals, it presents when polished a lustrous band running transversely across the fibres; and hence when cut *en cabochon* (*i.e.* with a convex surface) it is known as 'South African cat's-eye.' Large quantities are cut and polished in the Oberstein-Idar district (*v.* AGATE), where it is generally termed *Tigerauge*, if brown, and *Falkenauge*, if blue. As artificial methods of modifying the natural colour are practised, a considerable diversity of tints is now obtainable.

An analysis of this brown tiger-eye stone by F. Wibel gave  $\text{SiO}_2$ , 57.46;  $\text{Fe}_2\text{O}_3$ , 57.56;  $\text{H}_2\text{O}$ , 5.15 (N. Jahrb. f. Min. 1873, 367). His analysis of the blue variety yielded  $\text{SiO}_2$ , 97.27;  $\text{FeO}$ , 1.67;  $\text{CaO}$ , 0.15;  $\text{H}_2\text{O}$ , 0.57. The sp.gr. of the brown is recorded as 3.03; and of the blue 2.69. From microscopic examination of thin sections Wibel concluded that the ordinary brown mineral is a mixture of colourless fibrous quartz and *Göthite*, while the bluish variety is a mechanical aggregate of quartz and crocidolite. The fibrous quartz was regarded in both varieties as pseudomorphous after crocidolite.

A very careful study of these substances was made in 1884 by A. Renard and C. Klement (Bull. Ac. Roy. Belg. 3, 8), whose conclusions differed essentially from those of Wibel. Their analysis of the brown tiger eye yielded  $\text{SiO}_2$ , 93.03;  $\text{Fe}_2\text{O}_3$ , 4.94;  $\text{Al}_2\text{O}_3$ , 0.66;  $\text{CaO}$ , 0.41;  $\text{MgO}$ , 0.26;  $\text{H}_2\text{O}$ , 0.76. This comes nearer to the original analysis of Klaproth, who obtained  $\text{SiO}_2$ , 98.5;  $\text{Fe}_2\text{O}_3$ , 1.5. The blue hawk's-eye was found by Renard and Klement to contain  $\text{SiO}_2$ , 93.15;  $\text{Fe}_2\text{O}_3$ , 2.41;  $\text{FeO}$ , 1.13;  $\text{Al}_2\text{O}_3$ , 0.23;  $\text{CaO}$ , 0.13;  $\text{MgO}$ , 0.22;  $\text{H}_2\text{O}$ , 0.82. Their microscopic study of the stone leads them to conclude that the quartz is not a pseudomorph after fibrous crocidolite, but was deposited between the fibres of the original crocidolite from a siliceous solution which permeated the mineral. The rocks in which it is found have unquestionably been much altered.

Both the true crocidolite and the pseudo-crocidolite, or association of quartz and crocidolite, occur with jasper and magnetite in thin seams, more or less contorted, intercalated in the jaspideous schists of the Asbestos Mountains and the Doornberg. It is the fibrous crocidolite, formerly mistaken for asbestos, which has given the name to the Asbestos Mountains.

F. W. R.

**CROCIN** *v.* GLUCOSIDES.

**CROCOISITE.** Native lead chromate *v.* CHROMIUM.

**CROOKESITE** *v.* THALLIUM and SELENIUM.

**CROTON OIL** *v.* OILS.

**CROWN GLASS** *v.* GLASS.

**CRUCIBLES.** A perfect crucible should withstand the highest temperatures without fusion, should bear sudden changes of temperature without fracture, and should be unacted upon by the materials which are to be heated in it.

Clay crucibles are prepared from selected clay; of the Stourbridge clay worked, only about 5 p.c. is available for this purpose. Its plasticity is much increased by exposure for some months in a moist condition to the air. During this process of 'weathering' it becomes disintegrated and the removal of foreign matter is thereby facilitated. The presence of iron pyrites is especially injurious; furnace gases convert it into

<sup>1</sup> K. E. Schnitze has found 1:3:5 and 1:2:4 xylenol in the coal tar fraction 170-210° (B. 20, 410), and it is therefore reasonable to suppose that xylenols exist in 'cresylic acid,' although not yet detected in it.

the oxide which acts as a flux and forms cavities in the crucible. Lime is also hurtful, except when in very small quantities and uniformly distributed. Potash and soda are invariably present in clay, and when in small quantity increase the coherence of the crucible without appreciably impairing its power of withstanding the action of heat.

In order to reduce the tendency to crack, and to increase its refractory character, the clay is usually mixed with sand, ground flints, burnt clay (old broken crucibles), graphite or coke. These, which are either less fusible than the clay or altogether infusible, form a skeleton which upholds and prevents deformation of the crucibles at temperatures at which the clay would tend to fuse. The most refractory crucibles contain the largest proportion of silica.

The clay, which should be of the greatest possible fineness, is well beaten to remove air bubbles and mixed with the proper quantity of the refractory material. According to Berthier (*Traité des Essais*, 1, 66), when silica is used, it should not be too fine, as the tendency to combine with the clay and thus increase the fusibility would thereby be increased. Crucibles of fine grain are also more liable to fracture.

Small crucibles are usually baked in a kiln, but the large casting pots of Stourbridge clay are not baked until immediately before use. When the temperature of the baking is high, the crucible is more liable to fracture on reheating.

All clay crucibles are more or less acted upon by litharge, but metals and most ores may be heated in them without danger. Berthier recommends a lining of such material as silica, alumina, or magnesia previously moistened. A lining of chalk renders a crucible less permeable to litharge.

**Stourbridge clay crucibles** are made from a mixture of raw ground clay with about one half its weight of powdered, sifted, old glass pots, from which all adherent glass has been removed, the mixture being made in a disc mill, and kneaded to the proper consistency. Percy gives the composition of the Stourbridge clay used for the best crucibles as silica, 79.25; alumina, 13.57; iron oxide, 1.38; lime, 0.08; magnesia, 0.42; water, 5.11.

The following analyses show the composition of certain varieties of crucibles. Nos. 1-7 are by Berthier, No. 8 by Dick, Nos. 9-12 by Braud, and Nos. 13-15 by Mène :

—	Silica	Alumina	Iron oxide	Magnesia	Lime	Potash	Sulphur	Carbon	Water
1. French, made by Beaufay at Paris . . . . .	64.6	34.1	1.0	—	—	—	—	—	—
2. French, made by Deyeux at Savignics . . . . .	72.3	19.5	3.9	—	—	—	—	—	1.8
3. Hessian . . . . .	70.9	24.8	3.8	—	—	—	—	—	—
4. English steel . . . . .	71.0	23.0	4.0	—	—	—	—	—	—
5. St. Etienne steel . . . . .	65.2	35.0	7.2	—	—	—	—	—	—
6. Glass pots, Nemours . . . . .	67.4	32.0	0.8	—	—	—	—	—	—
7. „ „ Bohemia . . . . .	68.0	24.0	2.2	0.5	—	—	—	—	—
8. Cornish, made by Juleff . . . . .	72.39	25.32	1.07	trace	0.38	1.14	—	—	—
9. Steel crucible; clay . . . . .	53.92	40.57	—	—	—	—	0.23	—	—
10. „ „ coke clay . . . . .	42.78	34.71	—	—	—	—	0.49	18.60	—
11. „ „ graphite . . . . .	24.63	27.89	—	—	—	—	0.27	40.43	—
12. Magnesia . . . . .	4.8	2.49	—	92.62	—	—	0.099	—	—
13. English blacklead . . . . .	51.40	22.00	3.50	—	0.20	—	—	20.00	1.80
14. Ditto . . . . .	45.10	16.65	0.95	—	0.00	—	—	34.5	2.50
15. Ditto . . . . .	50.00	20.00	1.56	—	0.50	—	—	25.50	3.00

**Hessian crucibles** are composed of equal weights of almerode clay and sand. They are usually triangular, of coarse texture, porous, rapidly destroyed by litharge, and liable to fracture on sudden change of temperature, but will withstand a very high degree of heat.

**French crucibles** are made from a mixture of 1 part raw Ardennes clay and 2 parts of the same which has been burnt. They are refractory and of fine texture.

**Cornish crucibles** are largely used for copper assaying. They are round, of coarse grain, and of a mottled greyish-white colour. They are kiln-burnt, and withstand sudden changes of temperature, but cannot be heated to whiteness. Cornish crucibles are now made by the Morgan Crucible Company at Battersea.

**London crucibles** are of reddish-brown colour and close texture. They will not stand sudden change of temperature, but withstand the action of litharge fairly well.

**White fluxing pots** are made by the Morgan Company from a highly refractory fire-clay from Rozen. Crucibles containing carbon are now largely used. For very high temperatures, crucibles cut from a block of gas carbon or similar material may be employed. Clay crucibles may also be filled with a moist mixture of charcoal with starch, treacle, gum-water, or oil, or, for large crucibles, gas tar. The mass is forced with considerable pressure into the crucible and is then cut out, leaving a coating of about  $\frac{1}{8}$ -inch in thickness, or the coating is put into the crucible and smoothed with a glass rod. The crucible is then filled with powdered charcoal and heated to redness.

For the fusion of metals, *plumbago* or *coke* crucibles are of great value, but they are not largely used for assaying. At the Battersea works the following process of manufacture is employed:—Hand-picked Ceylon plumbago is ground, sifted, digested with dilute sulphuric



acid to remove the greater part of the iron, and mixed and kneaded to a stiff paste, with about an equal weight of fine fireclay. The mixture is passed through a pug-mill, and is cut into blocks. When required for use, the blocks are again passed through the mill, and made by hand on a wheel or moulded by machinery. They are then dried and baked in saggars.

**Graphite crucibles** are of fine grain, and will withstand the highest temperatures and repeated sudden changes. The graphite is slowly oxidised by metallic oxides or by the furnace gases. To minimise this, the crucible may be coated by dipping in a paste of clay and solution of borax. Any iron which is present in the graphite is liable to become introduced into the melt, and the carbon itself combines with iron or steel (*v.* Brand, C. C. 15, 407; and D. P. J. 256, 227).

**Salamander crucibles**, made by the Morgan Company, contain a much smaller proportion of carbon. They withstand sudden changes of temperature perfectly.

**Lime crucibles** are absolutely infusible. They are cut from blocks of well-burnt (preferably slightly hydraulic) lime. Their use in Deville's oxyhydrogen furnace is described under PLATINUM.

**Magnesia** was introduced by Caron as a refractory basic material for making crucibles or for lining reverberatory furnaces for melting and dephosphorising steel. Magnesia contracts considerably when heated; it is therefore necessary, before making it into bricks or crucibles, to expose it to a higher temperature than that to which it will be heated. The strongly calcined magnesia is made into a paste with 15-30 p.c. of raw (slightly calcined) magnesia, and 10-15 p.c. of water, and is moulded, dried, and baked at a red heat. The highly-heated magnesia would not cohere without admixture with the raw material. Magnesia crucibles are not injured by exposure to the atmosphere. Gaudin makes crucibles from a mixture of 1 part magnesia and 1 part bauxite.

**Alumina crucibles** withstand sudden changes of temperature, and are not affected by the materials fused, even sodium being without action. According to Deville's process (A. Ch. [3] 46, 195), alumina precipitated at low temperature from ammonia alum solution is mixed with an equal weight of powdered marble, and is exposed to the highest temperature of a wind furnace. The mixture so produced, which may be considered as consisting of calcium aluminate, is mixed with its own weight of moist, precipitated alumina, and is made into a crucible, dried and baked. When the crucible is required to withstand higher temperatures, the amount of the calcium aluminate may be reduced, but the proportion of lime should not fall below 10 to 20 p.c.

**Bauxite** has been used to replace alumina. It is extremely refractory (*v.* *Bauxite*, art. ALUMINIUM).

**Porcelain crucibles** *v.* PORCELAIN.

**Platinum crucibles** *v.* PLATINUM.

See further, Kerl, Handb. Thonvaaren Ind. 1879, 528-534; and Percy, Metallurgy (Fuel &c. 1875), 110-141.

**CRYOLITE.** (*Kryolith*, Ger.) A native fluoride of aluminium and sodium, found almost

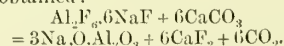
exclusively in Greenland, whence it has been sometimes called 'Greenland spar.' The name cryolite, or 'ice-spar' (*Eisstein*) refers to the general resemblance of the mineral to ice (*εἶσος*) and to its ready fusibility in a candle-flame. The mineral was discovered by the Danes in 1791, and described in the following year by Schumacher. Nearly all the cryolite of commerce is obtained from a single locality at Evigtok, about 12 miles from Arksut, in W. Greenland. This locality was visited by Giesecké, and later by J. W. Taylor (Quart. Jour. Geol. Soc., 12, 110). The cryolite occurs as a large deposit in gneiss, and contains (especially near its junction with the enclosing rock) a number of metallic minerals, such as galena, pyrites, and chalybite (*v.* P. Johstrup, N. Jahrb. f. Min. 1886, 1, Ref. 28).

Cryolite is usually found in cleavable translucent masses, of snow-white colour, with a vitreous lustre. H. 2.5; S.G. 2.9-3. Crystals are rare, and their relations have been the subject of much discussion. Formerly considered to be orthorhombic, they were afterwards regarded by Descloiseaux and Websky as triclinic, while recently Krenner and Groth have described them as monoclinic (Zeit. f. Kryst. 7, 1883, 375). Although cryolite is usually white, it is sometimes coloured brown or reddish, and is said to pass downwards, in the Greenland deposit, into a black mass. The black variety loses its colour when heated. BB. cryolite fuses to a white enamel.

The composition of cryolite may be represented by the formula  $\text{AlF}_3 \cdot 6\text{NaF}$ . This corresponds to 13 p.c. Al, 32.81 Na, and 54.19 F. An analysis of the Greenland cryolite by Chodnew yielded 13.23 p.c. Al, and 32.71 Na, with 0.83 of  $\text{Mn}_2\text{O}_3$  and MgO (Verh. Petersb. min. Ges., 1815-6, 209). Daruow found in the cryolite of Miask, in the Urals, 13.41 p.c. Al, 32.31 Na, 0.55  $\text{Fe}_2\text{O}_3$ , and  $\text{Mn}_2\text{O}_3$  and 0.35 CaO (P. 83, 587). Deville found in the Greenland cryolite 0.018 p.c. of vanadic acid and a small proportion of phosphoric acid. An analysis of cryolite from near Pike's Peak, California, by Cross and Hillebrand yielded Al 12.9, Na 32.4, F 53.55,  $\text{Fe}_2\text{O}_3$  0.4, Ca 0.28,  $\text{H}_2\text{O}$  0.3 (Am. J. S. [3] 26, 1883, 271).

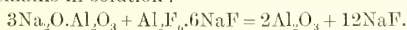
Cryolite was formerly a rare mineral, but about 1855 it was introduced into Europe commercially, and at once found numerous applications in the arts. By heating finely powdered cryolite with sodium, or with magnesium, J. Percy and A. Dick obtained metallic aluminium (P. M. 10, 1855, 364). H. Rose and Wöhler about the same time prepared aluminium by heating cryolite with KCl or NaCl. Deville found that fused cryolite is decomposed by the passage of an electric current, with elimination of free aluminium. At the present time aluminium is not obtained from cryolite, as the metal prepared in this way has been found to contain phosphorus.

A wide range of applications was suggested when Julius Thomsen showed in 1850 that cryolite is readily decomposed by ignition with carbonate of calcium, and that aluminate of sodium may be thus obtained:

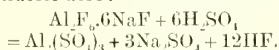


If ignited with quicklime, a similar decomposition is effected, of course without evolution of  $\text{CO}_2$ . The aluminate of soda has been used in

the manufacture of alum, and in the preparation of caustic soda for soap-making. By lixiviation, the aluminate is easily dissolved out; and by the passage of  $\text{CO}_2$  through the solution,  $\text{Na}_2\text{CO}_3$  is obtained, while alumina separates in a gelatinous form. The decomposition of cryolite may also be effected by boiling the finely-pulverised mineral with milk of lime. By adding an excess of powdered cryolite to the resulting solution, the aluminate is decomposed, the alumina being precipitated while fluoride of sodium remains in solution:



Cryolite can be readily decomposed by the action of sulphuric acid, with formation of sulphate of sodium, which can be easily converted into carbonate; but the process, after trial at Copenhagen, has been abandoned in consequence of the inconvenience arising from the evolution of hydrofluoric acid:



The manufacture of soda from cryolite is carried on at Oersund in Denmark, and at Natrona, near Pittsburg in Pennsylvania. The mineral is also employed in the preparation of an opaline glass, somewhat resembling porcelain. This glass may be formed by fusing together 100 parts of silica, 35 or 36 of cryolite, and 13 or 14 of oxide of zinc. C. Weinreb has investigated the cause of the milkiness of cryolite-glass, and believes that it is due to the presence of fluoride of aluminium, which on the cooling of the fused mass separates in a highly comminuted condition, and being distributed through the glass renders it more or less opaque (D. P. J., 256, 361). F. W. R.

**CRYPTOPINE** *v.* **VEGETO-ALKALOIDS.**

**CRYSOBERYL** or **CHRISOBERYL** *v.* **BERYLLUM.**

**CRYSTALLIN** *v.* **ALBUMINOIDS.**

**CRYSTAL PONCEAU** *v.* **AZO-COLOURING MATTERS.**

**CRYSTAL VIOLET** *v.* **TRIPHENYL METHANE COLOURING MATTERS.**

**CRYSTAL VARNISH** or **PAPER VARNISH** *v.* **VARNISH.**

**CUBEORE.** *Phasmasiderite; Siderite.* An iron arsenate found crystallised in cubes in Cornwall, Cumberland, France, Saxony, and Australia. Of an olive-green colour, passing into grass-green and emerald-green, or to honey-yellow and brown. Subtranslucent; sectile; pyro-electric. Sp.gr. 2.9. Hardness 2.5.

**CUBEBS CAMPHOR** *v.* **CAMPHORS.**

**CUBEBS, OIL OF,** *v.* **OILS, ESSENTIAL.**

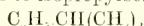
**CUDBEAR** *v.* **ARCHIL.**

**CULLEN'S EARTH** or **COLOGNE EARTH** *v.* **PIGMENTS.**

**CULET** *v.* **GLASS.**

**CUIM** *v.* **Anthracite, art. FUEL.**

**CUMENES.** *Cumols.* The name *cumene*, originally applied to isopropylbenzene



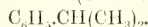
to indicate its connection with *cumic acid*, from which it was obtained by distillation with lime, is frequently employed as a generic term to denote any of the isomeric benzene hydrocarbons of the formula  $\text{C}_9\text{H}_{12}$ . Theory predicts the existence of eight of these, all of which are known.

### Propylbenzenes.

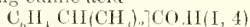
1. *Normal propylbenzene*  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ .

By the action of sodium on a mixture of bromobenzene and propyl bromide in ethereal solution (Fittig, Schäffer and König, A. 149, 324). From benzyl chloride  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  and zinc-ethyl (Paternò and Spica, B. 10, 294). Liquid boiling at  $158.5^\circ$  under 751.6 mm. pressure; sp.gr. 0.8702<sup>98</sup> (R. Schiff, A. 220, 93). Yields benzoic acid on oxidation.

2. *Isopropylbenzene (Cumene)*



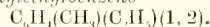
By distilling cumic acid



with lime or baryta (Gerhardt and Cahours, A. Ch. [3] 1, 87). From benzal chloride  $\text{C}_6\text{H}_5\text{CHCl}_2$  and zinc-methyl (Liebmann, B. 13, 46). From benzene and either isopropyl bromide or normal propyl bromide in presence of aluminium bromide (Gustavson, B. 11, 1251). Liquid boiling at  $152.5$ – $153^\circ$  (cor.); sp.gr. 0.87976 at  $0^\circ$ . Yields benzoic acid on oxidation.

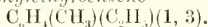
**Methylethylbenzenes.** The three methylethylbenzenes are obtained by the action of sodium on a mixture of the corresponding bromotoluenes (ortho-, meta-, or para-) with ethyl bromide or iodide.

1. *o-Methylethylbenzene*



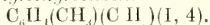
Liquid boiling at  $158$ – $159^\circ$ ; sp.gr. 0.8731 at  $16^\circ$ . Dilute nitric acid oxidises it to *o*-toluic acid  $\text{C}_6\text{H}_4(\text{CH}_3)\text{CO}_2\text{H}$  (1, 2).

2. *m-Methylethylbenzene*



Liquid boiling at  $158$ – $159^\circ$ ; sp.gr. 0.869 at  $29^\circ$ . Chromic acid oxidises it to isophthalic acid  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$  (1, 3).

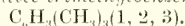
3. *p-Methylethylbenzene*



Liquid boiling at  $161$ – $162^\circ$ ; sp.gr. 0.8652 at  $21^\circ$ . Yields on oxidation *p*-toluic and terephthalic acids.

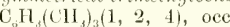
### Trimethylbenzenes.

1. *Consecutive trimethylbenzene*



By heating the calcium salt of  $\alpha$ -isoduric acid  $\text{C}_6\text{H}_3(\text{CH}_3)_3\text{CO}_2\text{H}$  with lime. Liquid boiling at  $163$ – $170^\circ$  (Jacobsen, B. 15, 1857).

2. *Unsymmetrical trimethylbenzene (pseudocumene)*

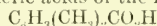


occurs together with mesitylene in coal-tar (Beilstein and Kögler, A. 137, 317). By the action of sodium on a mixture of either bromo-paraxylene or bromo-metaxylene with methyl iodide. In order to isolate it from coal-tar, Armstrong recommends (C. N. 38, 5; B. 11, 1697) that the mixture of pseudocumene and mesitylene (*v. infra*) boiling between  $160^\circ$  and  $170^\circ$ , obtained from coal-tar by fractional distillation, should be converted by treatment with an equal volume of concentrated sulphuric acid into sulphonic acids. The mixture of sulphonic acids, which separates as an oily layer on carefully adding water to the sulphuric acid solution, is heated with concentrated hydrochloric acid in a sealed tube for 1 hour at  $100^\circ$ . In this way the mesitylene sulphonic acid is decomposed, regenerating mesitylene, whilst the pseudocumene-sulphonic acid is not attacked. After separating the mesitylene the pseudocumene-

sulphonic acid is precipitated from the hydrochloric acid solution by sulphuric acid, purified by recrystallisation from dilute sulphuric acid and finally decomposed by heating with hydrochloric acid at 140–150°, when it breaks up into pseudocumene and sulphuric acid. Jacobsen (B. 9, 256) treats the mixture of sulphonic acids with barium or calcium carbonate, which removes the excess of sulphuric acid and converts the sulphonic acids into barium or calcium salts; transforms these by double decomposition with sodium carbonate into sodium salts; heats the latter with phosphorus pentachloride, with which they yield the sulphonic chlorides  $C_9H_7SO_2Cl$ ; converts the chlorides into the sulphonamides  $C_9H_7SO_2NH_2$  by the action of ammonia; and separates the two isomeric sulphonamides by recrystallisation from alcohol, in which mesitylene sulphonamide is readily, pseudocumene sulphonamide only sparingly soluble. The sulphonamides are then hydrolysed by heating with concentrated hydrochloric acid to 175°:

$$C_9H_7SO_2NH_2 + 2H_2O = C_9H_7 + H_2SO_4 + NH_3$$

Pseudocumene boils at 169.8° (cor.); sp.gr. 0.8643 at 0°. On oxidation with nitric acid it yields two isomeric acids of the formula



—xylic acid and *p*-xylic acid—and a small quantity of xylidic acid  $C_9H_7(CH_3)(CO_2H)_2$ .

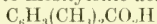
3. *Symmetrical trimethylbenzene (Mesitylene)*  $C_9H_7(CH_3)_3$  (1, 3, 5). In coal-tar (Fittig and Wackenroder, A. 151, 292). By distilling acetone with sulphuric acid

$$3CO(CH_3)_2 = C_9H_7(CH_3)_3 + 3H_2O$$

(Kane), or by dissolving allylene  $CH_2C=CH$  in sulphuric acid and distilling with water

$$3CH_2C=CH = C_9H_7(CH_3)_3$$

(Fittig and Sehrohe, B. 8, 17). (On the isolation of mesitylene from coal-tar and the method of separating it from pseudocumene *v.* preceding paragraph.) Liquid boiling at 164.5°; sp.gr. 0.8694  $\frac{98}{4}$  (R. Schiff, A. 220, 94). Dilute nitric acid oxidises it to mesitylenic acid



and utivic acid  $C_9H_7(CH_3)(CO_2H)_2$ ; with potassium permanganate it yields utivic acid and trimesic acid  $C_9H_7(CO_2H)_3$  (1, 3, 5). F. R. J.

**CUMIDINE**  $C_9H_{13}N$ . Of the eleven isomeric cumidines which have hitherto been obtained, pseudo- or  $\psi$ -cumidine and mesidine are perhaps the most important. These bases are derivatives of pseudocumene and mesitylene respectively, the first of which is theoretically capable of yielding three isomeric  $\psi$ -cumidines, and the latter one cumidine only.

**Pseudocumidine,  $\psi$ -cumidine,**

$(CH_3)_3C_6H_3.NH_2$  [ $CH_3:CH_2:CH_2:NH_2 = 1:3:1:6$ ], can be obtained by nitrating pseudocumene with fuming nitric acid in the cold, and reducing the nitro-compound (m.p. = 71°) with tin and hydrochloric acid (Schaper, Z. [2] 3, 12). The base is prepared technically by digesting xylidic hydrochloride with methyl alcohol in an autoclave at 280–300°, converting the crude product into the nitrate, separating the sparingly soluble nitrates by means of a centrifugal machine, washing the product with water and finally treating with an alkali. The mixture of bases consisting of cumidines and xylidines is then fractionated and the portion distilling between 225–245° is allowed

to crystallise, and finally freed from non-crystallisable bases by pressure (Aktiengesellschaft für Anilinfabrikation, German Patent 22,265). The cumidine so obtained contains mesidine and other impurities (Hofmann, B. 17, 1912; Engel, B. 18, 2229) but consists chiefly of Schaper's pseudocumidine (*cf.* Hofmann, B. 15, 2895) which can be prepared in the pure state by digesting  $\alpha$ -ortho-xylidine [ $NH_2:CH_2:CH_3 = 1:3:4$ ] or para-xylidine with methyl alcohol under similar conditions (Nölting and Forel, B. 18, 2680).

**Properties.**—Pseudocumidine crystallises in large, lustrous prisms, melts at 63° (Hofmann), at 68° (Auwers, B. 18, 2661) and boils at 231°. It is insoluble in water but readily soluble in alcohol. The nitrate is characterised by being very sparingly soluble in water. Its acetyl-derivative crystallises in compact white needles, melts at 161° (Edler, B. 18, 629; Nölting and Baumann) at 161° (Auwers) and boils above 360°. Pseudocumidine is used as a source of azo-dyes (German Patents 3,229 (1878), 2,265 (1882)).

$\psi$ -cumidine [ $CH_3:CH_2:CH_2:NH_2 = 1:2:4:5$ ] has been prepared by Edler (*l.c.*). It melts at 36°.

$\psi$ -cumidine [ $CH_3:CH_2:CH_2:NH_2 = 1:3:4:2$ ] is obtained by digesting  $\beta$ -ortho-xylidic hydrochloride [ $NH_2:CH_2:CH_3 = 1:2:3$ ] with methyl alcohol in an autoclave at 300° (Nölting and Forel; *cf.* Mayer, B. 20, 972). It boils at 240° (Nölting and Forel), 236° and does not solidify at –15° (Mayer). Its acetyl-derivative melts at 186°.

**Mesidine** [ $CH_3:NH_2:CH_2:CH_3 = 1:2:3:5$ ] is obtained by treating mesitylene with nitric acid (sp.gr. = 1.38) and reducing the nitro-derivative with tin and hydrochloric acid (Fittig and Storer, A. 147, 3). It can also be prepared by digesting  $\alpha$ -metaxylidine [ $NH_2:CH_2:CH_3 = 1:2:4$ ] (Hofmann, B. 5, 715; 8, 61) or  $\beta$ -metaxylidine [ $NH_2:CH_2:CH_3 = 1:2:6$ ] hydrochloride (Nölting and Forel) with methyl alcohol at 300°.

**Properties.**—Mesidine is a colourless liquid, which boils at 230° and has a sp.gr. = 0.9633. The acetyl-derivative melts at 216° and crystallises in prisms.

**Isocumidine**, prepared by digesting  $\gamma$ -metaxylidine [ $NH_2:CH_2:CH_3 = 1:3:5$ ] hydrochloride with methyl alcohol, at 300° (Nölting and Forel), melts at 67–68°, boils at 245°, and yields an acetyl-derivative melting at 163–164°.

**Paramidopropylbenzene**, formed by heating aniline, propyl alcohol, and zinc chloride at 280° for 8 hours (Louis, B. 16, 105; Francksen, B. 17, 1221), boils at 224–226°. The acetyl-derivative melts at 87°.

**Paramidopropylbenzene** (Louis, B. 16, 111; *cf.* Nicholson, A. 65, 58) boils at 216–218°.

**Ethylorthotoluidine**, prepared by treating orthotoluidine, ethyl alcohol, and zinc chloride at 270° (Benz, B. 15, 1650), boils at 229–230°. The acetyl-derivative melts at 105–105.5°, and boils at 313–315°.

Bases isomeric with these have also been described by Tafel (B. 19, 1930), Fileti (G. 13, 379), and Engel (B. 18, 2229).

**CUMIDINE PONCEAU.** *Cumidine red v.* AZO-COLOURING MATTERS.

**CUMIDINE RED v.** AZO-COLOURING MATTERS.

**CUMIN, OIL OF, v.** OILS, ESSENTIAL.

**CUMOLS v.** CUMENES.

**CUPRITE.** *Copper suboxide v.* COPPER.



CUPROPLUMBITE *v.* LEAD.CURARA. *Curare, Uriari, Wourari, Wourali,*

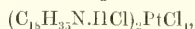
*Wourara.* Curara is the arrow poison of those tribes of South American Indians which inhabit the districts lying between the Amazon and the Orinoco. It was first brought to Europe by Sir Walter Raleigh in 1595, and from that time to this its origin and preparation have been much discussed by travellers and botanists. A summary of the earlier observations of La Condamine, A. v. Humboldt and Bonpland, Waterton, Schomburgk, Castelnau, Weddell, Thirion, Jobert, Crévaux, and others is given in a recent examination of the subject by Planchon (Ph. [3] 11, 469, 491, 529, 589, 693, a. 751). It is shown that curara is an aqueous extract of a mixture of many plants, one of which is always a species of *Strychnos*, and gives to it the chief toxic power, while the remainder contribute those other qualities which render the extract suitable for the tipping of arrow-heads. The method of preparation adopted by one tribe of Indians is described by Schomburgk (Ph. [3] 10, C16). The product differs somewhat with the locality in which it is prepared. Planchon distinguishes four varieties: the curara of the Orinoco, of the Upper Amazon, of French Guiana, and of British Guiana. The chief active ingredient in the preparation of the first is a *Strychnos* plant, closely allied to Bentham's *S. torifera* (J. Ph. 1882, (5) 5, 20), of the second, *S. Castelnauana* (Weddell), of the third, *S. Crévauxii* (Planchon), and of the fourth, *S. toxifera* (Benth.).

As seen in Europe, curara is a brown to black, nearly solid, or even brittle, extract. It has a bitter taste, and in its poisonous action it is related, though opposed, to strychnine. In medicine it has been employed in the treatment of tetanus, epilepsy, and hydrophobia. It is best administered hypodermically in the form of aqueous solution (*cf.* Moss, Ph. [3] 8, 421). The active part of curara is soluble in cold water, and constitutes three-fourths of the whole. This portion is nearly insoluble in alcohol, and quite insoluble in ether (Sachs, A. 191, 255).

A more or less definite and active alkaloidal product of curara under the name *curarine* was described by Roulin and Boussingault (A. Ch. [2] 39, 24), A. v. Humboldt (A. Ch. [2] 39, 30), Pelletier and Pétroz (A. Ch. [2] 40, 213), Pryer (Z. 8, 381; Bl. [2] 4, 238), Dragendorff (Z. [2] 3, 28), and Flückiger (N. R. P. 22, 65). Evidence of the same constituent in the root bark of *S. torifera* has been obtained by Villiers (J. Ph. [5] 11, 653). Pryer announced the discovery not only of crystalline salts of curarine, but of the base itself in a crystalline form, for which he proposed a formula. These results are, however, rendered doubtful by the experiments of Sachs (A. 191, 251), which show that Pryer's crystalline curarine sulphate consisted of calcium phosphate, together with traces of carbonate and mechanically adhering curara, to which last its slight physiological activity is ascribed. Moreover, Pryer's formula, though derived from an undoubted platinum salt of curarine, is erroneous on account of the salt having suffered decomposition.

Sachs prepared a number of salts of curarine by precipitation from a solution of the acetate, which solution he obtained as follows. A solu-

tion of potassium mercuric iodide was added to a cold aqueous solution of curara, and the precipitate which formed was collected. After washing, it was suspended in water and treated with sulphuretted hydrogen, which removes the mercury, while the alkaloid goes into solution. Lead acetate was then employed to separate the iodine, and finally the excess of lead was precipitated by sulphuretted hydrogen. The *platinum salt* obtained from this solution by the addition of platinic chloride and hydrochloric acid is pale yellow, and has the composition



but changes rapidly with the formation of a violet-coloured compound of a different composition. The *gold salt* also quickly decomposes. Neither the sulphate nor the hydrochloride are crystallisable. The most stable and best-defined salt is the *picrate*  $C_{15}H_{33}N.C_6H_2(OH)(NO_2)_3$ , from which Sachs deduces the formula  $C_{15}H_{41}N$  for the free base. He also points out that the alkaloid exists in the extract combined with sulphuric acid.

Boehm (B. 20, 144R.) treats the aqueous solution of curara directly with platinic chloride, and by a series of operations, in which the presence of free mineral acid is avoided, obtains the *free base* as an amorphous yellow, or in thicker layers orange-red, powder. If an aqueous solution of this powder, which has a green fluorescence, be evaporated with a little dilute acid, there result crystals of a physiologically inactive *compound* not yet further examined.

Curarine salts, according to Peliken (A. Ch. 44, 507), Pryer, Flückiger, and others, give a colour reaction with potassium dichromate and sulphuric acid similar to that of strychnine, but more permanent. Their behaviour towards solvents, especially water and benzene, serves to distinguish them from strychnine salts (Flückiger). Sachs obtained a red and not a blue colour by treating curarine salts with sulphuric acid, contrary to the statements of Pryer and Flückiger (*cf.* S. C. I. 1889, 176). For extraction of curarine in poisoning cases *cf.* Koch (C. C. 1871, 219) and Salomon (Fr. 10, 454).

Boehm (B. 20, 143R.) announces the discovery of a non-poisonous alkaloid *curine* in curara. It constitutes, indeed, the chief part of that extract, and being only sparingly soluble in water, is found partly in the aqueous solution together with the curarine, and partly in the residue. From the latter it is extracted by dilute sulphuric acid, and from either solution it is precipitated by ammonia. The precipitate is extracted with ether, the ether removed, and the residue extracted with alcohol, and the alcoholic solution precipitated by water. Thus obtained, curine is a white crystalline or amorphous powder, very slightly soluble in cold water, soluble in alcohol and chloroform, and less so in ether. It melts at 160°, and in solution gives a characteristic voluminous precipitate with metaphosphoric acid. The *platinum salt* contains 19.3 p.c. Pt. It is noteworthy that while itself inert a *new base* is obtained by treating curine with methyl iodide that is exceedingly poisonous, acting in a manner similar to curarine.

A. S.

CURARE *v.* CURARA.CURARINE *v.* CURARA; VEGETO-ALKALOIDS.

S S

**CURCUMIN** or **NEW YELLOW** or **CITRONIN**. A mixture of nitrated diphenylamine orange with nitrodiphenylamine.

**CURCUMIN** v. **TURMERIC**.

**CURCUMIN S** v. **STILBENE**.

**CURINE** v. **CURARA**.

**CUSCAMINE** v. **VEGETO-ALKALOIDS**.

**CUSCONINE** v. **VEGETO-ALKALOIDS**.

**CUSPARIA BARK**. *Angostura bark*; *Carony bark*. (*Ecorce d'Angusture*, Fr.; *Angostura-Rinde*, Ger.) The bark of the *Galipea Cusparia* (St. Hilaire), a tree inhabiting the mountain districts drained by the Orinoco (cf. Benth. A. T. 43). Confusion has sometimes occurred between cusparia and nux vomica bark. The two barks may, however, be readily distinguished by treatment with a drop of nitric acid, which either deepens the colour of the cusparia or gives it a bluish shade, while nux vomica, similarly treated, exhibits a blood-red colour. Several other barks have from time to time been substituted for true angostura. For these, and the mode of detecting them, v. Pereira (Mat. Med. 3rd ed. 2, 1915); Maisch (Am. J. Pharm. 1874, 50); Cazeneuve (Rép. de Pharm. 1874, 261); Oberlin a. Schlagdenhauffen (Pharm. Zeit. 1878, 853).

Among early analyses of cusparia, those of Pfaff and Fischer (Pereira) are the most important. These observers find in the dried bark 90 p.e. of lignin together with gum, resins, volatile oil, and a peculiar bitter extractive. The bitter extractive, examined in 1833 by Saladin (J. de Chim. Méd. 9, 388), was found to contain a crystalline neutral to which the name *cusparin* or *angosturin* was given. This substance is said to melt at 45°, to be soluble in alcohol, sparingly soluble in water, and to be precipitated by a solution of tannic acid. The existence of this compound has not been confirmed by subsequent investigators. The *volatile oil* of cusparia has been studied by Herzog (Ar. Ph. [2] 93, 146; J. 1858, 414) and by Oberlin a. Schlagdenhauffen (J. Ph. [4] 26, 130). The bark yields 0.2 p.e. of oil. It boils at 266–267°, has a sp.gr. 0.934, and has a dextrorotatory power of +5.4°. Its composition is  $C_{12}H_{20}O$ , and it is probably a mixture of a hydrocarbon and an oxygenated oil. An alkaloid, *angosturine*,  $C_{10}H_{10}NO_{11}$ , differing from the cusparin of Saladin, was isolated by Oberlin and Schlagdenhauffen (J. Ph. [4] 28, 263). It melts at 85°, is crystalline and bitter. It gives with sulphuric acid a red, and with sulphuric and nitric acids a green colour. Another *cusparine* was found in the bark by Körner and Böhringer (G. 13, 363), who announce the discovery of several new basic and acid constituents. The cusparine of these chemists has the composition  $C_{10}H_{11}NO_3$ . It is crystalline, and melts at 92°. It is sparingly soluble in ether, but soluble in alcohol. The sulphate, oxalate, and hydrochlorate are only sparingly soluble in water. The platinum salt consists of orange-yellow crystals. Treated with potassium hydroxide, cusparino breaks up into a new crystalline *alkaloid* and an aromatic crystalline *acid*. The mother-liquors from which cusparine is obtained contain another alkaloid, *gallipeine*  $C_{20}H_{21}NO_3$ . It consists of white needles, melting at 115.5°. The salts are more soluble than the corresponding salts of cusparine. The sulphate contains

7H<sub>2</sub>O. It melts at 50°, and at 100° breaks up into the sulphate of a new *alkaloid* and a crystalline compound, containing nitrogen, and melting at 196°. The platinum salt of gallipeine crystallises in prisms. A third base, melting at 180°, was also obtained. It is sparingly soluble in ether, but may be crystallised from alcohol. Its salts, when in solution, exhibit a blue fluorescence.

Cusparia is employed in medicine as a tonic in such derangements of the alimentary canal as dyspepsia, diarrhoea, and dysentery.

A. S.

**CUTCH**. *Terra japonica* v. **CATECHU**.

**CYANIDES**. Compounds of the radical NC or 'Cy.' For the production of combined cyanogen the following reactions, among others, are available:—

(1.) A mixture of acetylene and nitrogen, in contact with an alkali, is exposed to the action of a spark-current.  $C_2H_2 + N_2 = 2NCH$  (Berthelot). Ammonia is passed over red-hot charcoal  $2NH_3 + C = NCH.NH_3 + H_2$  (Langlois).

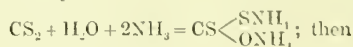
(2a.) In the presence of potassium carbonate, potassium cyanide is produced (Scheele).

(3.) Dry nitrogen is passed over a mixture of charcoal and alkali, or barium carbonate, at a red heat. The basylous metal unites with nitrogen and carbon into cyanide. Barium carbonate works best, although it is not reducible to metal by charcoal alone (Desfosses, Fownes, Bunsen, and Playfair).

(4.) Metallic potassium is heated with charcoal containing nitrogen—i.e. nitrogenous animal-matter, or the char derived from such matter, is fused with potassium carbonate; potassium cyanide is produced. This is the only reaction which is used at all extensively in chemical industry. For its rationale v. *Prussiate of potash*.

(5.) Carbon bisulphide and ammonia are made to act upon one another in dilute alcoholic solution. Ammonium thiocyanate is produced (Millon). The presence of alcohol is not absolutely essential.

Probably in the first instance,



the H<sub>2</sub>S uniting with the surplus ammonia.

Of technically available sources of ready-made cyanogen, we may mention

(1.) The tar-water produced in the making of gas from coal, which contains ammonium cyanide and thiocyanate, and the crude gas, which contains ammonium cyanide.

(2.) The volatile products formed in iron-smelting, which, as Bunsen and Playfair showed, include a very noteworthy proportion of potassium cyanide.

Of the large number of cyanides, the one known as yellow prussiate of potash is the most important for us here, because it serves as a starting-point for the preparation of the rest.

**Yellow Prussiate of Potash**. (Ger. *Blutlaugensalz*.) *Potassium ferrocyanide*  $Cy_4Fe.K_3.3H_2O$ .

*History*.—The pigment called *Prussian blue* was discovered accidentally by a colour-maker, Diesbach of Berlin, about the beginning of last

century. The chemist Dippel found out a method for its production, which is to fuse blood-solids with carbonate of potash in an iron vessel, to lixivate the fused mass with hot water, to add ferrous (and ferric) salt to the solution, and to acidify with mineral acid. The blue separates out as a precipitate. It was found subsequently that any kind of nitrogenous animal matter, if taken conjointly with finely divided iron, acts like blood-solids. Scheele made the important discovery that Prussian blue, if boiled with caustic potash ley, yields a precipitate of ferric hydrate and a solution of the potash salt of the acid of which the blue substance is the ferric salt. This potash salt, which forms the essential component of *Blutlauge*, Scheele found, can be precipitated from its aqueous solution by means of alcohol. The salt became known as *Blutlaugensalz*, which name has currency in Germany to the present day. (For further historical information, *v. Bibliography*, 1.)

For the manufacture of yellow prussiate, we, of course, need not produce Prussian blue and decompose it, as Scheele did; it suffices to evaporate *blood-ley* to crystallisation, to collect the crystals formed, and to purify them by re-crystallisation. This method, indeed, is used almost exclusively at the present day. None of the numerous other processes which have been proposed in the course of time has been found to be commercially successful.

*Manufacture of Prussiate of Potash.*—The raw materials used are:—

(1.) Carbonate of potash as extracted from wood-ashes, or made by the Leblanc process from native chloride.

(2.) Iron filings or borings.

(3.) Some kind of nitrogenous animal matter, or the char produced from such matter by dry distillation. The following list gives the names of the most frequently used materials, and their average percentages of nitrogen, according to Karmrodt (*Bibliography*, 4):—

	Percentage of nitrogen.
Horn . . . . .	15 to 17
Charred horn (50 p.c.) <sup>1</sup> . . . . .	7
„ (30 p.c.) . . . . .	4 to 5
„ which has gone through the fusion process once	0.5 to 0.75
Ox-blood dried . . . . .	15 to 17
Woollen rags, good quality (up to)	16
„ bad quality (about)	10
„ good quality (75 p.c. char)	12.5
Woollen rags, good quality (25 p.c. char)	1.5 to 2
Sheep's wool, waste . . . . .	16 to 17
Hair of oxen, cows, and calves . . . . .	15 to 17
Pig's bristles . . . . .	9 to 10
Feathers . . . . .	17
Old shoes . . . . .	6 to 7
Leather cuttings, from tanners . . . . .	4.5 to 5
Bone charcoal . . . . .	1

Bone charcoal, however, is practically out of the question, nobody would care to use it. On the other hand, 'suint' (that complex of things

<sup>1</sup> The residue left if horn be charred until it is reduced to 50 p.c. of its original weight.

mostly soluble in water, which, when wool is being washed with water, passes away from it) might be added to our list, although it is of importance rather as a source of carbonate of potash than as one of organic nitrogen. Suint, if weighed dry, amounts to about one-third of the weight of the wool. According to Märker and E. Schulze (*Bib.* 6) it contains 38 to 41 p.c. of inorganic matter (carbonic acid deducted), and 58 to 60.5 of organic matter, including 1.9 to 3.4 of nitrogen, of which latter 0.06 to 0.18 are present as ammonia. The analyses of the ashes of two different samples gave: Potash,  $K_2O$ , 59, and 63.5 p.c.; soda,  $Na_2O$ , 2.8, and a mere trace; carbonic acid, 25.8 and 25.4; mean 25.6, corresponding to 80.3 of carbonate,  $K_2CO_3$ .

P. Havrez, in 1870 (*Bib.* 7), recommended suint for making prussiate of potash. In the works of Peltzer at Verviers it was used experimentally in conjunction with wool-refuse. The liquor obtained by lixiviation of the melt contained, for every 100 parts of carbonate of potash (originally employed in the shape of suint?), 17.3 of potassium cyanide, equal to 19 of prussiate. From the raw wool imported into Great Britain from Australia alone an immense quantity of potash might be recovered as prussiate or in other forms, but it is questionable whether this would pay, because potash nowadays is so very cheap. At present suint is used very largely (perhaps chiefly?) for the making of *lanoline*.

*The fusion process*, in former times, used to be carried out in pear-shaped cast-iron muffles, suspended over a fire, as shown in fig. 1. Suint

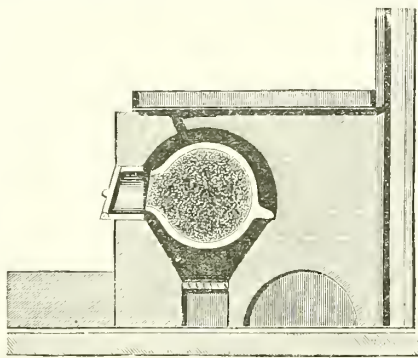


FIG. 1.

able dimensions are: Length, 1.2 metres; breadth, 0.8 m.; strength of body, 12 to 15 centimetres. In most works, however, these vessels have been replaced by shallow iron dishes, 1 to 1.8 metres in diameter, 10 centimetres deep, and 10 centimetres strength of body, which form the soles of reverberatory furnaces (fig. 2). A door at the side of the furnace, which is opened only when necessary, enables the pan to be charged, and the fused mass to be ladled out, at the end of the operation.

In the customary practice the carbonate of potash and the iron are introduced first; when complete fusion has been established, the animal matter, which must be as free from water as



possible, is introduced in instalments, with constant agitation. With wool, horn, and similar materials equal weights of animal matter and alkaline carbonate are usually employed; but the proportions vary very much, even for the same kind of animal matter, from one worker to

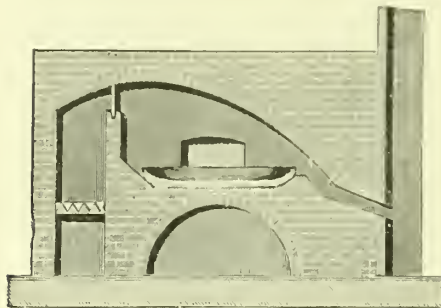


FIG. 2.

another. When all the animal matter is incorporated, the heat is raised, the furnace closed, and, finally, the thinly-fluid mass is ladled out into iron basins, where it solidifies into a hard black mass, known as *metal*. A fusion, as a rule, takes about three hours. The furnace-gases are utilised for heating the lixiviation and the evaporation pans.

In the open-pan system care should be taken that the flame is of a reducing character, because fused cyanide takes up oxygen and becomes cyanate; but the large volumes of combustible gases evolved during the process aid in protecting the melted mass against furnace gases and atmospheric oxygen.

The *lixiviation* of the metal is effected in flat iron pans at a temperature near the boiling-point of water. It lasts about nine hours. The insoluble black residue is washed systematically, and the wash-waters are used for subsequent extractions.

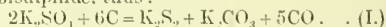
The solution, in addition to prussiate, contains large quantities of potassium carbonate and sulphide, and also more or less of potassium thiocyanate. It is evaporated to 32° Beaumé = 1.279 sp.gr., and allowed to cool, when a very impure prussiate crystallises out. The mother-liquor is evaporated further (to 32° B.) and a second crop of still more impure prussiate obtained. The last mother-liquor is evaporated to dryness and the residue calcined, to produce a very impure carbonate of potash known as *blue salt*, which is utilised in subsequent fusions. The impure prussiate is dissolved in hot water, and the hot-saturated solution is allowed to cool very slowly in iron tanks, within which strings are suspended or stretched out to encourage crystallisation. A small proportion of red prussiate is sometimes added, to impart to the crystals a darker shade than their natural colour, in order to please customers.

The commercial salt is, as a rule, contaminated with potassium sulphate, which is not easily removed by re-crystallisation. As this impurity does not interfere with any of the industrial applications of the salt, the manufacturer makes no great effort to remove it. A

laboratory method is, to add to the solution as nearly as possible the right amount of barium acetate, to remove the barium sulphate by filtration, and, from the concentrated filtrate to precipitate the prussiate by addition of alcohol.

Pure prussiate of potash crystallises from its aqueous solution in, as a rule truncated, quadrate octahedra; the crystals are very soft and of a lemon-yellow colour. Their sp.gr. is 1.83. The crystals are stable in air at the ordinary temperature; at 60° the water begins to go off, but complete dehydration demands long continued exposure to 100°, or to higher temperatures. The salt stands considerably higher temperatures without decomposition. It dissolves in 4 parts of cold and in 2 parts of boiling water. The light-yellow solution, when exposed to the light, is slowly decomposed, with formation of a blue precipitate of a cyanide of iron. If the solution is boiled in the presence of air (is the presence of air essential?), it gives off ammonia very slowly, and becomes alkaline. Though a cyanide, prussiate of potash is *not* poisonous.

The *theory of the prussiate process* was elaborated by Liebig (Bib. 2), partly on the basis of experiments, to which Reinhold Hoffmann subsequently furnished a valuable supplement (Bib. 5). The animal matter, if heated by itself, would yield a residue of nitrogenous charcoal, a cyanide of carbon as one might call it. But potassium carbonate, together with carbon, at a red heat, represents so much potassium; this potassium unites with the *quasi* cyanogen of the charcoal into cyanide of potassium. The volatile part of the organic nitrogen may furnish some cyanogen, and probably does so, but in the ordinary mode of working most of it goes into the chimney as ammonia and nitrogen. But the animal matter invariably contains combined sulphur, and the pearl-ash, as a rule, is contaminated with potassium sulphate, and this salt, when heated with charcoal, yields potassium bisulphide, thus:

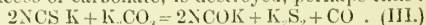


which, by the action of the potassium cyanide, is reduced to mono-sulphide,  $K_2S$ ; hence there are two reasons why the potassium cyanide should, in part, pass into thiocyanate. This salt, indeed, is always present in the leys derived from the metal. It has been asserted by many chemists that the metallic iron added in the fusion-process reduces the thiocyanate to cyanide. Nöller especially asserted that this was so (Bib. 8), but Reinhold Hoffmann denied it in this sense at least that under manufacturing conditions the reduction fails to take place (Bib. 5); and all subsequent experience substantially confirms Hoffmann's view.<sup>1</sup>

In regard to the part played by the thiocyanate in the fusion process, R. Hoffmann records some curious observations. As found by him, potassium cyanide and potassium sulphate, if fused together, yield thiocyanate and cyanate, presumably thus:

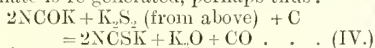


Now potassium thiocyanate, if fused with a large excess of carbonate, is destroyed, perhaps thus:

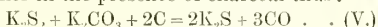


<sup>1</sup> Liebig, in a sense, to a qualification; see p. 633, 1st column.

but, if the mass is again fused with charcoal, thiocyanate is re-generated, perhaps thus:

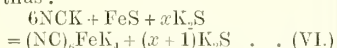


and, as charcoal is always present, thiocyanate once produced is not destroyed by the carbonate. But the formation of thiocyanate from the sulphate of pearl-ash can be prevented by fusing the alkali with iron and ordinary (wood) charcoal *before* adding the animal matter. By doing this we, in the first instance, realise eq. I.; but the bisulphide and the carbonate then act upon each other in the presence of charcoal thus:



Part of the potassium bisulphide produced (eq. I.), however, is decomposed by the iron with formation of a double sulphide of iron and potassium, possessing curious properties. It dissolves in hot water with formation of a dark-green solution; on standing in the cold the green solution assumes the form of a magma, the mother-liquor being almost pure water.

On re-heating everything passes into solution and the original green liquid is re-produced. On addition to it of a concentrated solution of carbonate of potash, the double sulphide is precipitated as such. Potassium cyanide solution does not act upon the solid double sulphide at all readily in the cold; but, if solutions of the two are mixed and heated, prussiate of potash is produced thus:



According to Hoffmann it is this reaction which, in the process of lixiviation, converts the cyanide of the fused mass into prussiate.

Liebig (Bib. 2) gives it as a result of experiment that metallic iron is dissolved by hot solution of potassium cyanide with evolution of hydrogen and formation of prussiate, and caustic potash; in the cold, if air be present, the potassium is eliminated likewise, but converted into potash by the action of atmospheric oxygen, without evolution of hydrogen.<sup>1</sup>

R. Hoffmann says of his double sulphide that it is decomposed by acids without elimination of sulphur and consequently must have had the composition  $\text{FeS} + x\text{K}_2\text{S}$ . It has, however, been since shown by G. Preiss (Bib. 9) that, by the fusion at high temperatures of finely divided iron (1 part), carbonate of potash (5 parts), and sulphur (5 parts), a crystalline double sulphide of the composition  $\text{Fe}_2\text{S}_3 \cdot \text{K}_2\text{S}$  can be produced; and supposing this sulphide to be produced in the prussiate process, the surplus sulphur in the  $\text{Fe}_2\text{S}_3$ , in the subsequent process of lixiviation, may give rise to the formation of thiocyanate at this stage. According to Preiss his (*ferric*) double sulphide is produced in the prussiate-fusion-process, if the temperature is sufficiently high; the leys are then clear-yellow, and yield relatively much crystallised prussiate; if the temperature is relatively low, a potassio-ferrous sulphide is produced, which is soluble in water with a green colour; it causes the formation of

green leys yielding relatively little prussiate. Preiss offers no experimental evidence to disprove Hoffmann's theory. We are inclined to think that Preiss's ferric double sulphide is produced in the prussiate fusion process (beside Hoffmann's), and, besides contributing towards the conversion of cyanide into prussiate, yields thiocyanate in the lixiviation stage. At any rate thiocyanate is produced invariably, and this in considerable quantity. R. Hoffmann reports on a long series of experimental fusions, made with a variety of animal matters, and sulphate-free pearl-ash or such ash and blue salt derived from such ash, on a manufacturing scale, and controlled by quantitative determinations. In the nine cases which he reports on, the ratios of cyanide of potassium present as prussiate to cyanide of potassium present as thiocyanate were, severally: 11·3; 11·6; 5; 7·4; 10·5; 13; 18; 6·7; 17·7 to one.

In connection with the conversion of the cyanide into prussiate, we may refer to a proposal of Habich's (Bib. 10), which is, to effect it by added powdered iron-spar,  $\text{FeCO}_3$ . If the ore is contaminated with lime or magnesia, he proposes to remove these by digestion with ferric chloride solution. Carbonate of iron, Habich says, acts more readily and exhaustively on the cyanide solution than any other kind of ferrous compound, and besides eliminates the the potassium in the convenient form of carbonate.

Of the very large excess of potash used in every individual fusion, a considerable portion comes back to the manufacturer in the form of blue salt. Karmrodt (Bib. 4), in a valuable memoir on the prussiate process, gives the results of a complete analysis of a blue salt derived from six weeks' working. He found in 100 parts:—

Potassium carbonate, $\text{K}_2\text{CO}_3$ . . .	52·75
Potassium silicate, $\text{SiO}_2 \cdot 2\text{K}_2\text{O}$ . . .	16·57
Potassium sulphide, $\text{K}_2\text{S}$ . . .	6·18
Potassium oxide, $\text{K}_2\text{O}$ . . .	7·22
Potassium prussiate, $(\text{NC})_6\text{FeK}_1 + 3\text{H}_2\text{O}$ . . .	2·82
Potassium chloride . . .	1·15
Potassium phosphate, $\text{K}_3\text{PO}_4$ . . .	2·04
Potassium sulphate . . .	4·34
Potassium thiocyanate . . .	a little
Insoluble matter, chiefly silica . . .	3·86
Organic matter, loss and errors . . .	3·07

100·00

A glance at this analysis shows that blue salt is practically a very impure pearl-ash; but, apart from this, it does not by far cover the loss of alkali involved in the fusions. In other words, the prussiate maker, in the course of a year, say, has to buy considerably more potassium in the form of carbonate than he sends out in the shape of prussiate. The causes of this loss have been ascertained by Hoffmann. Very little carbonate is lost by volatilisation. At the temperature prevailing in the fusion-pan potassium chloride volatilises very freely, but carbonate and sulphate do not; if potassium sulphate is found in the flues, this was produced from what were originally potassium chloride and ammonium sulphate. The lost potash, according to Hoffmann, must be

<sup>1</sup> I have tried to realise the first of Liebig's reactions as a lecture experiment, but failed to observe a visible evolution of hydrogen, and even to obtain prussiate; ordinary sulphide of iron, as used for the preparation of sulphuretted hydrogen, also yielded no prussiate in my hands.

searched for in the black sludges left after lixiviation of the metal by water, which contain abundance of potassium in the relatively insoluble form of potassio-sulphides of iron, and as part of insoluble silicates. Besides, some of the recovered *soluble* potash salt is silicate, which, in the sense of the prussiate process, is *not* equivalent to carbonate, being, unlike it, not reducible to potassium by the action of carbon at a red heat. In the successive recoveries of blue salt, the silicate, indeed, accumulates to such a degree that the salt from time to time requires to be de-silicated to become fit for use. If the black sludge be allowed to lie in the air, the sulphides of potassium and iron are oxidised, the former to sulphate, which can be extracted by means of water and thus recovered. Far more important, however, than the loss of potash is the loss of nitrogen involved in the process. In connection with this subject, Karmrodt (Bib. 4) records an interesting series of experiments. In each of the fusions referred to, the alkali used consisted of 500 pounds of pearl-ash, or of 100 of ash and 400 of blue salt, or of 150 of ash and 350 of blue salt.

1. Average result of ten fusions, each made with 500 pounds of best woollen rags. Total nitrogen used = 800 lbs. Total prussiate obtained = 761 lbs.; nitrogen in the prussiate = 152 lbs. Hence, nitrogen recovered as prussiate = 19 p.c. of the nitrogen employed.

2. Set of ten fusions, each with 500 lbs. of clean horn. Nitrogen recovered = 20 p.c.

3. Set of ten fusions, each with 500 lbs. of cows' hair. Nitrogen recovered = 15 p.c.

4. Set of ten fusions, each with 600 lbs. of leather cuttings. Nitrogen recovered = 32 p.c.

5. Set of ten fusions, each with 400 lbs. of horn-char, containing 7 p.c. of nitrogen. Nitrogen recovered = 58 p.c., showing that the charred material gave a greater proportion of its nitrogen as prussiate than any of the several kinds of natural animal matter. The nitrogen recovered as prussiate, it is true, amounts to only 12.6 p.c. of that contained in the 8,000 lbs. of horn from which the 4,000 lbs. of char were derived (the horn was the same as that which served for exp. 2, and the char weighed half as much as the original horn); but, if we adopt the rule of first charring a substance and using only the char for the fusion process, the large quantities of nitrogen, which in the charring escape as ammonia &c., need not be allowed to go up the chimney. For the utilisation of the ammonia of the vapours, Karmrodt recommends to pass them at a red heat over a reagent which he calls *Kohlenkali* and which he prepares as follows: 20 parts of carbonate of potash are dissolved in 10 parts of hot water, and the solution is mixed with the washed but undried precipitate produced from 8 parts of ferrous sulphate by addition of 6 parts of carbonate of potash, 30 parts of charcoal in pieces of the size of a hazel-nut are added to the magma, and the whole is made thoroughly dry over a charcoal fire. Karmrodt constructed a small experimental furnace which enabled him to distil a given material and pass the vapours through a red-hot column of *Kohlenkali*. The product was worked up into prussiate and the latter determined (by direct weighing of the crystals or by analytical

determination of the (NC)Fe in the solution produced?). In a set of five experiments, in each of which 3 lbs. of commercial ammonium carbonate were used, the nitrogen recovered as prussiate amounted, on the average, to 35.7 p.c. of the nitrogen present in the carbonate of ammonia by analysis. In each of another set of experiments 10 lbs. of *Kohlenkali* were used in conjunction with 3 lbs. = 96 Loth of horn. Nitrogen used in all = 16 Loth; nitrogen recovered as prussiate = 21 Loth or 45.7 p.c. of the total nitrogen in the horn employed. These results certainly were encouraging, but we are not aware that Karmrodt's process was ever used, even by himself, on a manufacturing scale.

Some time before Karmrodt, Brunquell (Bib. 3), also a manufacturer of prussiate of potash, had published a critical investigation of the prussiate process. After having pointed out the shortcomings of the customary process, and especially those of the fusion-pan, he recommends, as a good modification, to convert any unwieldy animal matters into char before use, and then to use this char in conjunction with richly nitrogenous, compact, and well-dried (uncharred) animal matter. Good proportions for the generality of cases, according to him, are—200 lbs. of pearl-ash (or 133 of blue salt and 67 of fresh carbonate), 40 of char, 130–140 of clean and dry uncharred animal matter, 16 of iron borings. The alkali is fused over a brisk fire, and the iron and the half of the char are next added with constant stirring. The heating is continued until a peculiar kind of smoke is seen to rise from the fused mass. The animal matter is now added, and, lastly, the second half of the char. In the ordinary process the greater part of the nitrogen of the animal matter goes away as ammonia. Brunquell proposes to save part of it as cyanide by a modified construction of the fusion apparatus. Instead of the customary pan he recommends a combination of two communicating egg-shaped iron pots superposed upon one another, and so suspended in a *gas-furnace* that they can be heated independently of each other. Each of the two pots has a disc-shaped stirrer, that of the upper has a tube for a rod; the rod of the lower passes through this tube, so that either of the two discs can be agitated by itself. The lower pot is charged with alkali and natural animal matter, the upper with alkali and *charred* animal matter, and the heating process is so conducted that the contents of the upper pot are in a state of fusion before those of the lower have lost much of their volatile matter. The lower pot is then heated, and the ammoniacal vapours produced there are compelled to bubble through the fused mass in the upper pot, which gives their nitrogen a good chance of conversion into cyanide. An imitation of the projected apparatus was made out of a tall crucible and charged with leather-char above and blood-solids below. The yield of prussiate was 33.2 p.c., of which 28.6 were found in the lower part of the crucible.<sup>1</sup>

An apparatus based on the same idea as Brunquell's was patented in 1883 by C. Engler

<sup>1</sup> This probably means 33.2 parts per 100 of animal matter used as such or as leather-char. The ordinary yield, according to Brunquell, is about 10 for every 100 of animal matter used.



and C. Bader (Ger. Pat. No. 23,132; v. W. J. for 1833 for a woodcut of their apparatus).

The real function of the added iron, Brunnquell quite correctly says, is to retard the destruction of the iron pan, which otherwise would have to supply all the iron for the iron sulphide unavoidably formed. He quotes a statement of Fleck's, that a pan wrought without iron stood only 100 fusions, while two other similar pans wrought with iron stood 343 and 405 respectively.

To complete our account of proposed improvements on the old prussiate process we must refer to a proposal made by Bramwell in 1855 (Bib. 29), which is to substitute sulphate for the carbonate used in the fusion process, and along with it a sufficiency of iron to eliminate the alkali metal from the sulphide produced from the sulphate by the action of the charcoal. It does not appear that Bramwell's process was ever tried even experimentally. Bramwell recommends sulphate of 'potash or soda,' which implies that, supposing alkaline sulphate not to work, soda-ash might be substituted for the more expensive carbonate of potash. Wagner, in reporting on Bramwell's paper, suggests the employment of a mixture of the two carbonates, which, as is well known, fuses more readily than either alone. By properly adjusting the proportions, he says, one might produce the salt  $(\text{NC})_2\text{Fe}, \text{KNa}_2$ , which crystallises very readily.

There can be no doubt that for most practical purposes soda-prussiate would be fully equivalent to the customary potash salt; but we have no right to take it for granted that carbonate of soda is as active a cyanogen-former as carbonate of potash. L. Possoz (Bib. 31) made a series of comparative experiments on a manufacturing scale with the two alkalis, and found that while, for instance, 100 parts of horn when fused with potash yielded on an average 25 parts of prussiate of potash, they yielded only 5 parts of prussiate of soda when soda-ash was used. An experiment recorded by R. Hoffmann in his memoir (Bib. 5) gave a different result. In one of his experimental fusions he used soda-ash instead of carbonate of potash, and, from 100 parts of woollen rags by fusion at a very high temperature obtained ferrocyanogen equal to 11 parts of prussiate of potash crystals, as against the 10 to 14 which he had obtained in a series of fusions with pearl-ash.

In 1880 S. Tanatar of Odessa (Bib. 32) took up the question and tried to decide it by laboratory experiments. He used blood-char (*carbo sanguinis*) as a source of nitrogen, and found that it gave only traces of cyanide when fused with iron and carbonate of soda. But when he added certain diluents to the mixture he obtained better results.

The following is an extract from his table of results:—

*Ten grams of blood-char and iron borings—*

(1) When fused with 25 grams of carbonate of potash gave cyanide equal to 2.15 grams of crystallised prussiate.

(2) When fused with 25 grams of carbonate of soda gave 0.2 grams of prussiate of soda.

(12) When fused with 25 grams of sodium chloride and 5 of carbonate of soda gave 2.17 grams of prussiate.

(13) When fused with 25 grams of sodium chloride, 5 of carbonate of soda, and 3 of carbonate of lime gave 2.3 grams of prussiate.

The numbers given are the averages of from 3 to 5 fusions. Mixtures 12 and 13 were tried with a kilogram of wool, and were found to give more cyanogen than the same material did with carbonate of potash. Unfortunately, Tanatar says, the crystallisation of the sodium salt from the leys offers great difficulties.

*Assay of the metal.*—It is obviously important for the prussiate maker to have a method for the rapid determination of the percentage of prussiate obtainable from a given metal. Of the many methods proposed Erlenmeyer's is probably the most exact (Bib. 11). He extracts a weighed sample with water with addition of ferrous sulphate and, if necessary, enough caustic soda to maintain an alkaline reaction, and removes the insoluble matter by filtration. From the filtrate he precipitates the ferro-cyanogen by an excess of ferric chloride in the presence of an excess of hydrochloric acid, as Prussian blue, which he filters off, washes, and decomposes by means of caustic potash. The ferric hydrate is filtered off and the ferro-cyanogen determined in the acidified filtrate by titration with potassium permanganate, according to De Haen's method. The *sulphocyanogen* of the metal is in the filtrate from the Prussian blue, and can be determined after further acidification, if necessary, by titration with permanganate.

$\text{NCS.H} + \text{O}_3$  (as permanganate) gives  $\text{NCH} + \text{SO}_3$  (+manganous salt).

This latter method of titration, however, does not give perfectly constant results even with pure solutions, and it is questionable whether it gives at all trustworthy results in the case here under consideration.

E. Bohliger (Bib. 12) determines dissolved alkaline ferrocyanide by titration with a standard solution of copper sulphate, the addition of which is continued until a strip of filter-paper dipped into the mixture no longer becomes blue when a drop of ferric chloride is put on it. Any sulphide present in the solution must first be removed by boiling with lead carbonate and filtering.

J. Müller (Bib. 13) and K. Zulkowski (Bib. 14) titrate with zinc sulphate. According to the latter, constant results can be obtained only with *hot* solutions. A suitable standard solution is obtained by dissolving one-fourth

$(\text{ZnSO}_4, \text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}) = 111.0$  grams

of this double salt in water and diluting to one litre. To test a 'metal,' 50 grammes of it (coarsely powdered) are digested in 150 c.c. of water, which at first causes considerable evolution of heat. After the mixture has cooled down to 40°C., this temperature is maintained for about two hours. The whole is then diluted to 250 c.c., filtered through a dry filter, and part of the filtrate put into a burette. 10 c.c. of the zinc solution are now measured out, mixed with 5 c.c. of dilute sulphuric acid (1 to 5) and 20 c.c. of water, and the whole is heated to boiling. 'Metal' solution is run into the hot liquid until, when a drop of the mixture is put on a piece of filter paper and a drop of very dilute ferric chloride solution put on the zone of paper

soaked in the solution (the precipitate remains localised in the place where the drop was put down) it just produces a blue colour. The liquid then, according to synthetical trials made with known weights of pure prussiate, contains seven times  $(\text{NC})_2\text{FeK}_3 + 3\text{H}_2\text{O}$  of added prussiate for every  $10 \times \text{ZnSO}_4$  used, plus 0.5 milligram of prussiate for every cubic-centimetre of mixture; i.e., supposing the total volume of the mixture at the end to be = V c.c., it contains

$$0.740 + 0.0005 \times \text{V grams}$$

of prussiate, whence the percentage is easily calculated. But the process had better be manipulated as a purely empirical one, i.e. after a preliminary determination of the strength of the 'metal'-solution, the exact weight of prussiate of potash which, under the circumstance which prevailed in this analysis, is equivalent to 10 c.c. of the zinc-solution, should be determined directly by means of an imitation of the metal-solution derived from an exactly known weight of pure prussiate. For the determination of the thiocyanate in blood-ley, Zulkowski adds excess of sulphurous acid to destroy the sulphide and lets this reagent act from half a day to a whole day. The acid liquid is then neutralised by addition of oxide of zinc and the ferrocyanogen fully precipitated by addition of excess of zinc sulphate. The filtered liquor is concentrated over a water-bath, and the thiocyanogen precipitated by addition of excess of copper sulphate and sulphurous acid, as cuprous thiocyanate,  $\text{NCS.Cu}$ , which is filtered off and weighed as such (after drying at  $100^\circ$ ), or ignited in hydrogen to be weighed as  $\text{Cu}_2\text{S}$ . Of the several processes of analysis here referred to, Zulkowski's is the most plausible; yet, according to experiments made in Professor Thorpe's laboratory by Dyson, it gives only moderately exact results (private communication from Prof. Thorpe).

#### PROPOSED NEW METHODS FOR THE MANUFACTURE OF PRUSSIAE OF POTASH.

None of these has had more than a very brief existence. They all agree in this, that they discard the use of animal matter and substitute for it either atmospheric nitrogen or ammonia.

Of the numerous attempts to produce cyanides from the nitrogen of the atmosphere, that of Possoz and Boissière (Bib. 15) is probably the earliest, and not the least successful. Charcoal, impregnated with 30 p.c. of its weight of carbonate of potash, is kept at a red-heat in fire-clay cylinders, through which a mixture of nitrogen and carbonic oxide, produced by passing air over red-hot alkalinised charcoal, is passing. The maximum amount of cyanide is formed after about ten hours. The process is continuous; while finished product is withdrawn from below (and made to cool in close iron boxes), fresh charges are introduced from above. The product is lixiviated with water in the presence of powdered spathic iron ore, to produce a solution of prussiate which is worked up as usual. The inventors, after having wrought their process in Grenelle, near Paris, without a profit, transplanted it to Newcastle, and there, for a time, produced as much as 1,000 kilograms of prussiate in a day. But the method could not compete with the old process, and the works were eventu-

ally closed. Bramwell simplified the process by utilising as nitrogen the gases of the furnace in which the cylinder is heated.

In 1861, Margueritte and De Sonrdeval (Bib. 16) established the important fact that baryta is a better basic reagent for causing the union of nitrogen and carbon into cyanogen, than carbonate of potash. A mixture of carbonate of baryta, iron filings, coal-tar and sawdust is ignited strongly in a fire-clay retort, when most of the baryta is reduced to oxide. A current of air, de-oxygenated by hot carbon, is then passed over the mass at a red-heat, when barium cyanide is formed in abundance. From this other cyanides are, of course, easily made, but the inventors, it appears, prefer to use it for the generation of ammonia, by the decomposing action of steam at  $300^\circ$ ,  $\text{Ba}(\text{CN})_2 + 4\text{H}_2\text{O} = 2\text{NH}_3 + \text{H}_2 + \text{CO} + \text{BaCO}_3$ .

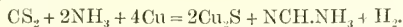
About 1881, V. Adler, having found that the formation of cyanogen from charcoal, nitrogen, and basic oxides is greatly facilitated by the presence of finely divided iron or other metal capable of combining with carbon and transferring it to the nitrogen and basifluous metal, sought to base upon this a new method for the manufacture of cyanides. We refer to the literature quoted under 17.

A long time ago Bunsen suggested to make potassium cyanide by constructing a kind of iron blast-furnace and working it with alternate layers of carbonate of potash and coal. The potassium cyanide produced might be let out from time to time from tap-holes provided at the proper places. We quote from W. J., 1855, p. 85, where the *Handwörterbuch der Chemie* [4], 273, is referred to.

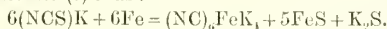
For the conversion of ammonia into cyanogen, one method is to pass it over red-hot charcoal, when vapour of ammonium cyanide is produced. Langlois (Bib. 18), who was the first to study the reaction, recommends it as the best method for the preparation of pure crystals of this salt. Kuhlmann (Bib. 19) utilised it experimentally for the preparation of prussiate of potash, by passing the gaseous product obtained by heating charcoal in a current of dry ammonia into a solution of caustic potash containing suspended ferrous hydrate, and obtained encouraging results. Brunnquell tried to use the reaction for converting the ammonia of the vapours resulting from the dry distillation of animal matter, ultimately, into prussiate of potash. Finding it impracticable to decompose ammonium cyanide by means of caustic potash, he proposes to pass the vapours containing the ammonium cyanide into a solution of ferrous sulphate, to produce ammonium sulphate and a precipitate of ferrous cyanide, which latter he collects and turns into prussiate by treatment with solution of potassium carbonate (Bib. 3). His ingeniously constructed apparatus for the absorption of the cyanide-vapours is described and figured in W. J., 1856, 110. On Karmrod's attempts in the same direction we reported above (p. 630).

A slight modification of Karmrod's process (addition of iron filings to the 'Kohlenkali') was patented by H. Johnston for Lucas in 1862 (Bib. 20). More original is the process of H. Schwartz (Bib. 21) who passes a mixture of ammonia and carbon bisulphide vapour over red-hot iron or copper, contained in an iron

tube, so as to form ammonium cyanide vapour, which he absorbs in a magma of ferrous hydrate and caustic-alkali-ley, and so produces ferro-cyanide.



Perhaps it is more correct to assume that in the first instance  $\text{CS}_2$  and  $2\text{NH}_3$  unite into  $\text{NCS.NH}_4 + \text{H}_2\text{S}$ , which are then both desulphurised by the copper. At any rate, the reaction here presumed does take place, as shown by Millon (Bib. 22), when carbon di-sulphide is kept in contact with aqueous ammonia solution. A. Gélis, in 1861 (Bib. 23), based upon this reaction a method for the industrial preparation of ammonium thiocyanate, and subsequently worked out a process for making potassium ferrocyanide from the thiocyanate (Bib. 24 and 25). Gélis's process for the manufacture of thiocyanate is considered below; his method for its conversion into prussiate is based upon the presumption that potassium thiocyanate, when heated with finely divided iron to dull redness, is decomposed with formation of *prussiate* (?) thus:



But this cannot be the case: even the possibility of producing potassium cyanide from thiocyanate profitably in this manner is more than doubtful. It certainly was at Gélis' time. (*v. supra* under R. Hoffmann). Payen, it is true, in his report says that the actual yield is about equal to that demanded by theory, but he offers no evidence on this point, and, supposing him to be right, why did the *Verein für die Beförderung des Gewerbfleisses in Preussen* as late as 1877 offer a prize of 1000 marks for the conversion of thiocyanates into prussiates? And why did Messrs. Günzburg and Tcherniac waste such an amount of time over the same problem?

Since about 1878 these two chemists, as appears from their publications, have been engaged in attempts to bring Gélis' processes into workable forms. Their apparatus and methods for the production of thiocyanates are described below under a special heading; we here confine ourselves to stating what they found out in regard to the problem of de-sulphurising thiocyanate of potassium. According to their experiments, this change can be effected satisfactorily by means of metallic iron, but only under the following conditions:—

(1) The thiocyanate must be dry and 'absolutely' pure. (What does 'absolutely pure' mean? They surely would not insist on *absolute* purity in the strict sense of the terms.)

(2) The iron must be clean and perfectly metallic. Ordinary 'reduced iron' is contaminated with more or less of protoxide, which, in the course of the fusion process, converts its equivalent of cyanide into the useless form of cyanate. 'Fer porphyrisé' on the other hand works admirably.

(3) The mixture of thiocyanate and iron must be very intimate.

(4) In the fusion process a temperature of as nearly as possible  $450^\circ\text{C}$ . must be maintained. Below  $350^\circ$  there is no action, while  $550^\circ$ , on the other hand, is a limit which it is dangerous to pass. (Why?)

The thiocyanate, after having been fused, and thus dehydrated, at  $300^\circ$ , is allowed to solidify, powdered finely and mixed with the iron powder in an apparatus so constructed that absorption of moisture from the atmosphere is precluded. The mixture is put into iron boxes with closely-fitting lids, and these are placed in a cast-iron chamber constructed like an ordinary laboratory steam-chest, but kept at  $450^\circ$  by means of boiling sulphur. (See fig. 3.) The sulphur-compartment communicates above with an upright pipe which acts as an inverted condenser. When the reaction is completed, the boxes are transferred to a chamber which can be closed hermetically and cooled down quickly by means of a current of cold water. The mass is treated with water, &c., *i.e.* manipulated exactly like ordinary 'metal.' It yields 'from 30 to 40

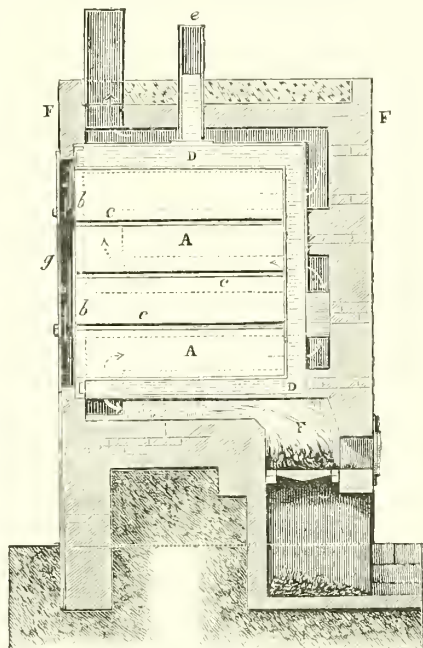


FIG. 3.

p.c. of crystallised prussiate,' Mr. Tcherniac (in his article 'Cyanures,' in the supplement to Würtz's Dictionnaire de Chimie) does not tell us what proportion of iron he uses; assuming he takes the calculated quantity, *i.e.* Fe parts of iron for NCS.K parts of the salt, the fused mass, by theory, should yield 45.9 p.c. of its weight of crystallised prussiate; the '30 to 35 p.c.' then would mean 'from 65 to 76 p.c. of the theoretical maximum.' Not a bad yield, surely, but would the process pay in practice? Besides, Tcherniac's numbers for the potential prussiate in his metals are probably too high, because he, no doubt, determined these analytically by means of his own process, which is as follows:

To analyse the solution derived from a given metal he begins by acidifying with sulphuric acid and next drops in strong solution of per-



manganate of potash, until the red colour remains for a few minutes. The mixture is allowed to stand for about half-an-hour to make sure that all the prussiate is converted into ferrieyanide and that the sulphide, thiocyanate, &c., are completely oxidised. (Tcherniac does not direct us to maintain a red colour in the mixture by occasional addition of more permanganate, but he no doubt means us to do so.) At last the mixture is made strongly alkaline by addition of caustic soda, heated to boiling and mixed with ferrous sulphate to re-convert the red into yellow prussiate with formation of magnetic oxide of iron, which is filtered off. The filtrate is acidified and its prussiate determined by titration with a standard solution of potassium permanganate (De Haen's method). The method, obviously, is based on the presumption that, in the first process of oxidation, the thiocyanate is converted into substances not susceptible of conversion into prussiate by treatment with ferrous hydrate and caustic alkali; but this, we believe, is a mistake; as shown by Erlenmeyer, permanganate, in acid solutions, converts thiocyanate into cyanide and sulphate, and the hydrocyanic acid, as far as it survives, will be reported as so much prussiate.

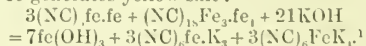
We have not the space for more than the bare outlines of a process for the production of prussiate from ammonium sulphate which was proposed by H. Fleck (Bib. 28). According to his experiments, if ammonium sulphate, sulphur, and charcoal are added to a fused mixture of potassium carbonate, sulphur, and charcoal, potassium thiocyanate is produced which contains one half of the nitrogen of the ammonia salt; the other half escapes as ammonia, along with sulphuretted hydrogen. If now iron filings be incorporated, a violent reaction sets in which leads to the formation of a black mass, equivalent to the 'metal' of the old process inasmuch as it yields prussiate on lixiviation with water.

**Red prussiate of potash or Ferrieyanide of potassium**  $(\text{NC})_6\text{FeK}_3$ . This salt was discovered by Leopold Gmelin in 1822. He prepared it by passing chlorine through solution of yellow prussiate until it no longer gave a precipitate or colouration of Prussian blue with ferric salt. The reaction is very simple: of the four atoms of potassium in yellow prussiate one is eliminated as chloride. Gmelin also found that the new salt gives a blue precipitate on addition of ferrous salt, which is similar to, but not identical with Prussian blue. The new blue subsequently became known as 'Turnbull's Blue.'

Gmelin's reaction is still used almost exclusively for the manufacture of the salt; only instead of passing chlorine through a solution of yellow prussiate, some prefer to chlorinate the powdered dry salt. In the latter case the mode of operating is either the same as in bleaching-powder-making, or else the powdered salt is placed in casks which are made to revolve while a current of chlorine is passing through them. The wet-way method, however, is more generally used and it must be, if the production of a pure preparation is contemplated.

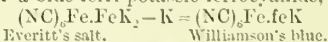
The fully chlorinated solution is evaporated to crystallisation, the red salt allowed to crystallise out and purified by re-crystallisation. The process is not so easy in practice as theory

might indicate. A solution of red prussiate if subjected to the action of chlorine, even in the cold, is slowly decomposed with formation of a green precipitate known as 'Prussian green,' which runs through any filter and prevents the formation of normal crystals. In practice it is, of course, quite impossible to avoid local excess of chlorine, and, as a consequence, the green precipitate makes its appearance before the whole of the yellow salt is converted into red. Posselt has discovered an easy mode of getting quit of this trouble. After having completed the chlorination, he evaporates to crystallisation (without heeding the green precipitate) and adds a little caustic potash to the hot liquor; the green compound is converted into ferric hydrate which is easily filtered off. Unfortunately, however, the process re-generates yellow salt:



Perhaps the best way out of the difficulty would be, to stop the chlorination as soon as the green precipitate threatens to form, and then to complete the change by the following process due to Williamson (Bib. 33):—

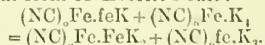
Everitt's salt (an insoluble ferro-potassic ferrieyanide which is formed in the preparation of hydrocyanic acid from prussiate of potash) is treated with an equivalent amount of nitric acid diluted with 20 parts of water, first in the cold, and then with cautions application of heat. The result of this operation is that the Everitt's salt loses half its potassium and assumes the form of a blue ferri-potassic ferrieyanide, thus:



Everitt's salt.

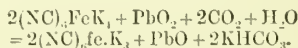
Williamson's blue.

The blue compound, when boiled with solution of potassium ferrieyanide, takes away one fourth of the potassium in the latter, and re-assumes its original form of Everitt's salt:



As the blue re-agent can be recovered from the Everitt's salt formed by means of nitric acid, Williamson's process would perhaps pay even as an independent industrial process for the preparation of the salt.

Schönbein recommended to make red prussiate by treating the solution of the yellow salt with lead di-oxide in the presence of carbonic acid:



The presence of excess of carbonic acid is essential, because red prussiate, monoxide of lead and caustic potash decompose one another in the sense of our equation as read from the right to the left. From the monoxide of lead the binoxide can be re-generated by means of bleaching-powder solution. Lunge (Bib. 35) recommends this combination of processes for the industrial manufacture of the salt.

Seuberlich (Bib. 36), as an improvement upon Schönbein's process, proposes to substitute hydrochloric for the carbonic acid.

Reichardt, of Jena (W. J. 1869, 270), effects

<sup>1</sup> Here, as also in the following section we use the symbol 'fe' as designating 56 parts of ferric iron, 'Fe' standing for the same weight of ferrous, or perhaps, of iron generally.

the conversion of yellow into red prussiate by means of bromine. The specific advantages claimed for the method are, that bromine is weighable and that an excess of it does not to anything like the same extent as one of chlorine lead to the formation of by-products.<sup>1</sup>

Reichardt's process would probably not pay industrially as it stands, but might perhaps be employed with advantage for completing a conversion which has already been almost accomplished by means of chlorine.

A method proposed by Rodger (Bib. 37) consists in preparing a mixed solution of ferric and potassic sulphates which contain the two bases in the exact proportion demanded by the formula for red prussiate, and then substituting 2 NC for every 1 SO<sub>4</sub> by precipitation with strontium cyanide.

Red prussiate of potash crystallises from water in magnificent dark-red monoclinic prisms which may assume a considerable magnitude. The crystals are anhydrous. Sp.gr. = 1.845 (Wallace). They dissolve largely in water, forming an intense yellow solution. (Yellow prussiate solution is only pale yellow.) At t° C. one part of the salt requires for its solution 'w' parts of water; the sp.gr. of the solution produced is 'S' (at t° ?).

t°	W	S
4.4 . . . . .	3.03	1.151
10.0 . . . . .	2.73	1.164
15.6 (60° F.) . . . . .	2.54	1.178
37.8 . . . . .	1.70	1.225
100.0 . . . . .	1.29	1.250
104.0 (boil. point) . . . . .	1.22	1.265

A solution of red prussiate gives a blue precipitate with solutions of ferrous salts (Turnbull's blue), which is insoluble in water and in mineral acids. With ferric salts it gives the intense brown colouration characteristic of ferric ferrieyanide.

A mixed solution of red prussiate and caustic potash is a powerful oxidising agent.

(NC)<sub>6</sub>Fe.K<sub>3</sub> + KOH = (NC)<sub>6</sub>Fe.K<sub>1</sub> + (OH, which effects the oxidations). Thus, for instance, indigo-blue is instantaneously decolourised by this combination of reagents.

**Ferrocyanic acid** (NC)<sub>6</sub>Fe.H<sub>1</sub> is produced when a solution of yellow prussiate is mixed with any of the stronger acids in the cold. For the preparation of a pure solution the barium salt is decomposed with the exact quantity of sulphuric acid, and the barium sulphate filtered off. A more convenient, but less exact, method is to decompose a strong solution of yellow prussiate by addition of the exact quantity of tartaric acid, which forms bitartrate with the

potassium of the salt. The bitartrate separates out on standing and is removed by filtration. For the preparation of *dry ferrocyanic acid*, a saturated solution of yellow prussiate, after removal of its absorbed air by boiling, is allowed to cool in the absence of air; a quantity of air-free ether is then added, and lastly, air-free hydrochloric acid. Ferrocyanic acid separates out in white scales, which are filtered off, washed with ether-alcohol, and purified by re-solution in alcohol and reprecipitation with ether. The preparation must be dried in the cold over oil of vitriol. A solution of ferrocyanic acid, if exposed to the air, and more especially at higher temperatures, suffers oxidation with formation of a blue precipitate, which, rightly or wrongly, is generally assumed to be Prussian blue. This reaction is utilised in calico-printing for the production of blue patterns.

If a solution of ferrocyanic acid is boiled, it is decomposed with elimination of half its cyanogen as hydrocyanic acid, NCH, and formation of an insoluble ferrocyanide of ferrosium and hydrogen.



A similar reaction takes place in the distillation of prussiate of potash with dilute sulphuric acid; only in this case the (NC)<sub>6</sub>Fe.FeH<sub>2</sub> first formed exchanges its two atoms of hydrogen for two of potassium from the potassium sulphate produced, and a precipitate of *Everitt's salt* (NC)<sub>6</sub>Fe.FeK<sub>2</sub> is left in the retort. Both precipitates are white, if pure, but they quickly absorb oxygen from the air with formation of blue compounds.

**Hydrocyanic acid.** Syn. *Prussic acid*. (Germ. *Blausäure*.) NCH or CyH. In a memoir published in the Transactions of the Swedish Academy for 1782-3 Scheele showed that the 'colouring principle' of Prussian blue can be isolated in two ways—viz. (1) by converting the blue into potash salt and distilling this with dilute sulphuric acid, and (2) by converting the blue into mercury salt by boiling it with mercury calx and water, precipitating the mercury by means of metallic iron and dilute sulphuric acid, and distilling the liquid decantate. In either case the 'principle' is contained in the distillate, as proved by the fact that the distillate, when mixed with excess of caustic alkali, ferroso-ferric salt, and excess of acid, regenerates Prussian blue. The body was subsequently called by Bergmann '*acidum cereulei Berolinensis*,' whence its familiar names, as given in the heading.

Scheele found that prussic acid itself is very volatile and combustible, and that one of the products of its combustion is fixed air. Combining this with the fact ascertained by him, that a mixture of wood-charcoal and pearl-ash yields no blood-ley salt when heated by itself, but does so if heated with sal-ammoniac, he concluded that prussic acid is composed of volatile alkali, fixed air, and phlogiston, which is in substantial accordance with our present views.

The exact quantitative composition of prussic acid (and the then known cyanides) was ascertained for the first time by Gay-Lussac in 1815. He showed that prussic acid is similar in its constitution to hydrochloric, hydriodic, and sulphydric acids, with, however, this important

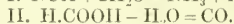
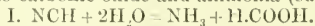
<sup>1</sup> In connection with this matter a very instructive research by Edgar J. Reynolds (C. J. for 1888, Trans. 767) may be referred to. Its principal result is that a saturated solution of red prussiate, if boiled with bromine (2 parts for one part of dry salt) under an inverted condenser for 5-6 hours, yields, amongst other things, a black fusible cyanide of iron of the composition Fe<sub>2</sub>Cy<sub>10</sub>, which behaves towards boiling caustic-potash ley as if it were a mixture Cy<sub>10</sub>.Fe<sub>2</sub>.Fe<sub>2</sub> + Cy<sub>10</sub>.Fe<sub>2</sub> of ferrium ferrocyanide and ferrieyanide, or, in other words, similarly to Prussian green, to which latter, indeed, some authorities assign the same formula as Reynolds does to his new compound (e.g. for instance, Roscoe-Schöerlemmer's Handbook of Chemistry). The new cyanide if exposed to moist air or washed with hot water loses ferrium as hydrate, and passes, very slowly, into Prussian blue.  
Fe<sub>2</sub>Cy<sub>10</sub> + 6H<sub>2</sub>O = Fe<sub>2</sub>(OH)<sub>6</sub> + Fe<sub>2</sub>Cy<sub>10</sub> + 6CyH.

difference—that the hydrogen in prussic acid is united, not with an elementary but with a ‘compound radicle,’ NC, which he called ‘cyanogène.’ Gay-Lussac thus for the first time introduced the notion of compound radicles, which, however, at his time, would have failed to take root in the minds of chemists if he had not succeeded in isolating this radicle (*v. infra*).

For the preparation of hydrocyanic acid the most convenient method probably is to decompose pure potassium cyanide with dilute sulphuric acid. The customary method is that of Scheele, which is to distil prussiate of potash with dilute sulphuric acid. For the preparation of an aqueous solution of the acid, 2 parts of oil of vitriol, 4–6 parts of water, and 3 parts of prussiate are suitable proportions to use. The prussiate, after having been coarsely powdered, is introduced into a retort, standing on a sand or asbestos bath; the neck of the retort, which is turned upwards, is connected with an efficient Liebig’s condenser by means of a glass elbow and perforated corks. The acid mixture is of course allowed to cool before it is poured on the salt. The distillation is continued until the residue is nearly dry. As prussic acid is very volatile and highly poisonous, it is as well to let the distillate go into a layer of water contained in the receiver, and to place the latter into cold water or, better, a mixture of ice and water.

The process, as we had already occasion to state, consists essentially in this—that one half of the cyanogen is liberated as NCH, while the rest of the elements concerned remain in the retort as Everitt’s salt and potassium sulphate. For pharmaceutical purposes the proportion of water is so adjusted that the distillate is decidedly, but not very much, above the strength prescribed by the Pharmacopœia, which in Great Britain is 2 p.c. of real NCH. The acid is then analysed and diluted down to the desired strength.

Anhydrous hydrocyanic acid cannot be made by distilling the prussiate with oil of vitriol, because this converts the NCH produced at once into carbonic oxide and ammonia (sulphate).



The strongest hydrochloric acid behaves similarly, except that the formic acid survives.

To prepare the real acid the handiest method is to pass its vapour through an inverted condenser, kept at say 30°C., and thence through a column of used calcium chloride kept at a similar temperature. Wöhler recommends to distil 10 parts of prussiate with 7 of sulphuric acid, diluted with 14 of water, in a retort, the neck of which is turned upwards, and connected in the first instance with a Woulf’s bottle containing a layer of pieces of erude calcium chloride, or lumps of common potassium cyanide, and through it with a large U-tube filled with fragments of fused calcium chloride, which must be free from powder. Both the Woulf’s bottle and the U-tube are immersed in water-baths kept at 30°, to prevent condensation of NCH. The dehydrated vapour is passed to the bottom of a tall narrow cylinder standing in a freezing mixture. The outlet tube must be pretty wide, because the anhydrous acid at low temperatures

is apt to freeze, which, in the case of a narrow tube, might lead to serious accidents. For the same reason, a glass spiral condenser surrounded by a freezing mixture cannot be used.

The substance NCH is a colourless mobile liquid, possessing a peculiar odour accompanied by a peculiar choking sensation in the larynx. We here, of course, refer, not to prussic acid vapour proper, but to air contaminated with mere traces of the vapour. The inhalation of anything like concentrated hydrocyanic acid vapour is fatal. The acid, indeed, is fearfully poisonous; a single drop of it, when placed on the tongue of a large dog, produces instantaneous death.

The sp.gr. of the liquid is 0.7058 at 7°, and 0.6967 at 18°C. (Gay-Lussac). According to the same authority it freezes at –15°; but Schulz asserts that the really anhydrous acid remains liquid at even –37°. The acid, under 760 mm. pressure, boils at 26.5°; at the low temperature of 4.5° its vapour tension is equal to half an atmosphere.

Hydrocyanic acid gas is inflammable, and burns into carbonic acid, water, and nitrogen. If kindled in the eudiometer with about the calculated volume of oxygen, it explodes very sharply.

The acid is miscible with water, alcohol, and ether in all proportions; in the case of water there is a fall of temperature accompanied by contraction (Bussy and Buignet). According to Gautier it forms a series of hydrates, and one of these—NCH + H<sub>2</sub>O—freezes at –22°. But all these hydrates are very unstable; aqueous hydrocyanic acid, on distillation, behaves like a mixture of the two components.

Hydrocyanic acid is but a feeble acid; it unites with even caustic potash only sluggishly, and the solution (of NCK) produced smells of the acid. It does not decompose carbonates or borates, nor does it act on sodium sulphate, which latter, by the action of hydrochloric acid, is converted into bisulphate with formation of sodium chloride. These facts afford methods for the separation of hydrocyanic from stronger volatile acids associated with it in the same solution.

Mercuric oxide is the only base on which hydrocyanic acid solution acts energetically and with formation of a very stable salt HgCy<sub>2</sub>.

For the quantitative analysis of a solution of hydrocyanic acid, the most exact method is to precipitate the cyanogen as silver cyanide from a known weight of the solution by means of silver nitrate, to collect the precipitate on a weighed filter, wash it, and weigh it after drying at 100°; but the method demands more time than the pharmacist can as a rule afford. More expeditious, and for practical purposes sufficiently exact, is the following titrimetric process of Liebig’s. The acid to be analysed is diluted largely with water and supersaturated strongly by addition of caustic potash. If the alkali should happen to be free from chloride, a trace of sodium chloride must be added to the mixture. This being done, a neutral standard solution of silver nitrate is dropped in from a burette until the cloud of silver chloride which appears locally from the first, by addition of the last drop of reagent, has become permanent on



stirring—i.e. until the reaction  $2\text{NCK} + \text{Ag}(\text{NO}_3 \text{ or } \text{Cl}) = \text{K}(\text{NO}_3 \text{ or } \text{Cl}) + \text{AgK}(\text{NC})$  has just been accomplished. From this equation it is easily calculated that 6.283 grams of pure silver nitrate, dissolved in water and diluted to 1,000 c.c., gives a solution of which 1 c.c. corresponds to 2 milligrams of real  $\text{NCH}$ .

A pure aqueous solution of hydrocyanic acid is subject to a peculiar kind of (as it appears) absolutely spontaneous decomposition, which involves the formation of richly carboniferous dark-coloured products. This decomposition, which sets in even in the absence of light and air, is greatly retarded by the presence of small proportions of hydrochloric or sulphuric acid. The anhydrous acid, if pure, is not liable to a similar change.

**Cyanogen** (Germ. *Cyan*)  $(\text{NC})_2$  was discovered by Gay-Lussac. It is prepared by heating perfectly dry mercuric cyanide in a retort or tube made of hard glass, when the cyanide breaks up into metal and cyanogen, which latter always suffers partial polymerisation into (non-volatile) paracyanogen. The cyanogen comes off as a gas characterised by a peculiar pungent smell and an irritating action on the nose and eyes.

It is readily inflammable and burns with a peach-blossom coloured flame into carbonic acid and nitrogen. If passed through a glass tube kept at  $-30^\circ$ , it condenses into a colourless liquid which according to Bunsen exhibits the following vapour-tensions:

$-20.7^\circ$ . . 1 Atm.	$+10^\circ$ . . 3.8 Atm.
$10^\circ$ . . 1.85 "	$15^\circ$ . . 4.4 "
$0^\circ$ . . 2.7 "	$20^\circ$ . . 5.0 "

Water absorbs about 4.5 times its volume of cyanogen gas, alcohol 23, and ether 5 times its volume. The solutions on standing soon become dark-coloured, and then contain ammonium oxalate, ammonium carbonate, prussic acid, urea, and numerous other products. A piece of potassium or sodium, if heated gently in cyanogen, readily unites with the gas forming alkaline cyanide. A solution of caustic potash absorbs it with formation of cyanide and cyanate, just as chlorine forms chloride and hypochlorite. Cyanogen gas is highly poisonous.

**Mercuric cyanide**  $\text{Hg}(\text{NC})_2$  is easily prepared by dissolving mercuric oxide in aqueous hydrocyanic acid and evaporating to crystallisation. It forms colourless anhydrous crystals, soluble in eight times their weight of cold water. This salt, for a simple cyanide, possesses an extraordinary degree of stability in presence of water; its solution remains unchanged on boiling, nor is it changed visibly on addition of caustic potash. This explains why most heavy metallic cyanides, including ferrocyanides amongst others, when boiled with water and oxide of mercury, suffer decomposition with elimination of the cyanogen as mercury salt, and of the heavy metal as oxide or hydroxide. Scheele's method for making mercuric cyanide out of Prussian blue may be quoted as an illustration.

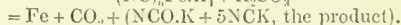
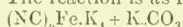
**Potassium cyanide**  $\text{K}(\text{NC})$ . This salt might be produced directly from nitrogenous animal matter by means of potassium carbonate in an impure state, but its purification would present insuperable difficulties. In the present practice

it is always made from yellow prussiate of potash. In theory the simplest method is to first dehydrate the salt and then to heat it to redness in the absence of air; the  $4(\text{NC})\text{K}$  assume the form of fused potassium cyanide, the  $\text{Fe}(\text{NC})_2$  is decomposed with formation of nitrogen (cyanogen?) and a black infusible solid which used to be looked upon as carbide of iron, but according to Terrell (Bib. 38), is rather a complex mixture. The percentage composition of a specimen analysed by Terrell was: Iron present as such 32.0, iron as  $\text{Fe}_2\text{O}_3$  27.6, free carbon 27.5, carbon combined with iron 1.17, carbon as  $\text{NC}$  0.21, nitrogen 0.30, potassium 0.8, oxygen 0.5.<sup>1</sup> If the fused mass be allowed to stand for a sufficient time at a temperature above its freezing point, the black compound settles, so that the fused cyanide can be decanted off. Unfortunately, however, the precipitate in many cases settles so very slowly that in practice some of it must be allowed to pass into the decantate. At first sight it would suggest itself to extract the cyanide from the fuse by means of water, but this is not practicable without regenerating part of the prussiate by the action of the cyanide solution on the ferrous precipitate. Nor will it do to use alcohol as a solvent, because an alcohol strong enough to preclude regeneration of prussiate dissolves potassium cyanide only very sparingly. Moreover, a pure solution of the salt cannot be evaporated to dryness undecomposed. A solution of potassium cyanide indeed smells of prussic acid, which proves that it contains free  $\text{KHO}$  and  $\text{NCH}$  side by side; on evaporation the prussic acid is evolved and a further instalment of salt is decomposed, so that, ultimately, a considerable quantity of caustic potash, or rather carbonate (by the action of the atmosphere) is produced. There is only one method for preparing pure potassium cyanide. We must prepare a strong alcoholic solution of pure caustic potash, and pass anhydrous or nearly anhydrous hydrocyanic acid vapour into it. The cyanide then comes down as a crystalline precipitate. This method was worked out long ago by Wiggers for laboratory purposes. L. Knaiff (Bib. 39) recommends it for the manufacture of the salt. Two parts of caustic potash, 'containing 4 equivalents of water,' are dissolved in 10 parts of alcohol of  $90^\circ$ ; on the other hand, 4 parts of prussiate are distilled with the (cooled) mixture of 3 parts of oil of vitriol and 7 of water, and the hydrocyanic acid vapour is passed into the alkali-solution. The crystalline precipitate is collected on a cloth filter, washed two or three times with  $90^\circ$  alcohol, and squeezed in a press. It is then dried slowly but completely at a gentle heat. At last the dry salt is fused by putting it, in instalments, into an iron crucible, previously heated to dull redness in a charcoal fire. The crucible, before use, must be made smooth inside by means of a lathe, and the fusion must be continued until a sample of the fused mass, as lifted out with a hot iron spatula, is white and transparent. The fused mass is then poured out into a smooth iron basin, broken up and at once transferred to well-stoppered bottles. The

<sup>1</sup> An analysis by Dyson, carried out in Professor Thorpe's laboratory some time ago, gave similar results, (Private communication.)

*Potassium cyanatum purissimum* of commerce is probably all made in this manner.

The ordinary commercial preparation is a mixture of cyanide with cyanate and other impurities. It is made by mixing 8 parts of anhydrous yellow prussiate with 3 parts of anhydrous potassium carbonate, projecting the mixture into a red-hot iron crucible and continuing the application of heat until the contents are in a state of tranquil fusion and a drop taken out by means of a hot wire is clear and transparent. The reaction is as follows:

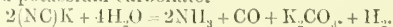


As the iron in this case assumes the form of *metal*, it settles more readily than the 'carbide' produced in the fusion of unmixed prussiate does, and a clear salt is more easily obtained by decantation. This way of making potassium cyanide is usually credited to Liebig, but it was, we believe, invented by F. and E. Rodgers (Bib. 40).

Rudolf Wagner proposes to substitute sodium carbonate 2 parts for the 3 parts of potassium salt, and in a later communication he recommends the addition of 0.5 part of powdered charcoal, which latter is probably intended to reduce the cyanate. The advantages claimed for the modification are the lower price of the sodium salt, that the mass fuses more readily, and the iron settles more promptly than it does in the original process. That part of the alkali-metal is sodium instead of potassium is of course no objection technically (Bib. 41, 42).

Erlenmeyer (Bib. 42) prepares cyanide free from cyanate by fusing anhydrous prussiate with the calculated proportion of metallic sodium.

Potassium cyanide, as obtained by synthesis, crystallises in colourless transparent cubes. The ordinary fused salt looks like glazed porcelain. It fuses at a dull red heat: at a white heat it is volatilised, undecomposed if air and vapour of water are absent. At a red heat, contact with dry air produces cyanate, and vapour of water forms (more quickly) ammonia, carbonic oxide, and potassium carbonate.



Potassium cyanide dissolves very largely in even cold water, the solution is strongly alkaline to test-paper, and smells of prussic acid (*vide supra*). When heated to boiling it is said to give off ammonia with formation of formate,  $(NCK + 2H_2O = NH_3 + H.COOK)$  but the writer's laboratory experience causes him to doubt whether formate is produced at all largely; at any rate he endeavoured in vain to prepare formate in this manner. If ammonia is evolved from hot solutions of potassium cyanide, this is probably due to the presence of cyanate. Dilute acids, even acetic (also carbonic to a certain extent) decompose the salt readily with formation of hydrocyanic acid. Concentrated sulphuric and hydrochloric acids act similarly, only the  $NCH$  produced is at once decomposed with formation of ammonia-salt and formic acid or carbonic oxide.

Potassium cyanide is used in the laboratory as a dry-way reducing agent (for the conversion of heavy metallic oxides and sulphides into metals), and in the wet way as a metal precipitant. It used to be employed largely in photo-

graphy as a solvent for silver salts. Its most important technical application nowadays is the preparation of certain heavy metallic double cyanides, which are used in electro-plating, and of which the most important are dealt with in the following section. Potassium cyanide and all the double cyanides except yellow and red prussiate and (presumably) cobaltcyanide of potassium are intensely poisonous.

### Metallo-cyanides of potassium.

**Gold salt.** Gold leaf dissolves in potassium cyanide solution in the presence of air as auro-cyanide  $AuK.(NC)_2$ , one half of the potassium of the original salt being converted into hydroxide (Elsner).<sup>1</sup> A method of preparation is the following: 7 parts of gold are dissolved in *aqua regia*, the solution is precipitated by ammonia, and the precipitate (fulminating gold), after having been washed, is thrown into a hot solution of 6 parts of potassium cyanide without separating it from the filter. The fulminating gold dissolves at once with evolution of ammonia, and the filtered liquor, if not too dilute, deposits on cooling colourless crystals of the double salt, which are easily purified by recrystallisation. The mother-liquor, which contains large quantities of potassium carbonate and chloride, yields no pure crystals on evaporation. To work it up, evaporate it with excess of hydrochloric or nitric acid to dryness over a water-bath and wash the residue with water in the dark. Yellow aurous cyanide  $AuNC$  remains. Dissolve 77 parts of this salt in a solution of 23 parts of potassium cyanide. According to Elsner, a solution good enough for electro-plating can be obtained as follows. A neutral solution of gold tetrachloride, derived from 28 parts of metal, is precipitated by addition of 210 parts of magnesia suspended in water. The precipitate of magnesia aurate produced is washed on a filter with water, and the magnesia is dissolved out with nitric acid. The washed gold oxide is dissolved in a solution of 500 parts of yellow prussiate in 4,000 parts of water.

From a solution of auro-cyanide the gold cannot be precipitated by sulphuretted hydrogen, but metallic zinc gradually brings it down as metal. A good quantitative method is to evaporate the solution over litharge to dryness, to fuse the residue after addition of potassium cyanide, and to cupel the regulus, preferably after addition of a little silver. The resulting gold-silver bead is 'parted' with nitric acid.

**Silver salt.** Silver cyanide dissolves readily in solution of potassium cyanide. The hot solution, if sufficiently strong, deposits colourless crystals of the salt  $AgK.(NC)_2$  on cooling. For electro-platers' purposes a solution of potassium cyanide containing 100 grams of the salt per litre is saturated with recently precipitated silver cyanide, and the filtered solution is mixed with its own volume of potassium cyanide solution.

**Copper salts.** Cupric cyanide, as produced by the addition of potassium cyanide to cupric sulphate, readily breaks up into cyanogen and

<sup>1</sup> Messrs. John S. MacArthur, R. W. Forrest, and Wm. Forrest, of Glasgow, having found that even very dilute solutions of the re-agent act on finely divided gold with a surprising degree of promptitude, have based upon this reaction a process for the extraction of gold from gold ores (British patent, 1887, No. 11,174).

cuprous cyanide, which latter makes its appearance as a white precipitate. Cuprous cyanide dissolves in solution of potassium cyanide with formation of compounds of the two cyanides, of which latter the following two are best known: (1) A prismatic salt,  $\text{Cu}_2(\text{NC})_2 \cdot 2\text{K}(\text{NC})$ ; this salt, by the action of water, is decomposed with elimination of cuprous cyanide and formation of the salt (2)  $\text{Cu}_2(\text{NC})_2 \cdot 6\text{K}(\text{NC})$  which forms rhombohedral crystals. Both salts are colourless. A solution available for electro-coppering may be prepared by first producing a washed precipitate of cuprous oxide and then dissolving it in solution of potassium cyanide.

### Ferro- and ferri- cyanides of iron.

Ferrous cyanide  $\text{FeCy}_2$ , and ferric cyanide  $\text{FeCy}_3$ , can hardly be said to be known. A compound of the two of the empirical composition  $\text{Fe}_2\text{Cy}_8$  was prepared lately by E. J. Reynolds (*vide supra*). A variety of ferro- and ferri-cyanides of iron or of iron and alkali metals can be produced by the interaction between solutions of ferro- or ferri-cyanide of potassium on the one hand, and iron salts generally on the other.

1. *Ferrocyanide and ferrous salt.* If potassium ferrocyanide be poured into an excess of solution of ferrous chloride (or sulphate), a white precipitate is produced which is generally assumed to be identical with 'Everitt's salt,'  $\text{Cy}_6\text{FeFeK}_2$  (*v. supra*).<sup>1</sup> Whether or not, its behaviour to atmospheric oxygen and oxidising agents generally is similar to that of Everitt's salt. The exact nature of the blue body produced on exposure of either of the two bodies to the air has, we believe, never been ascertained; the change produced in Everitt's salt proper by nitric acid has been studied by Williamson, who, as we had already occasion to state, found that it consists in the first instance in the elimination of half of the potassium as nitrate, and the consequent formation of an insoluble blue substance which we will designate as 'Williamson's blue.' Williamson's blue is a ferri-cyanide of ferrous and potassium  $\text{Cy}_6\text{FeFeK}$ . Boiling solution of yellow prussiate of potash reconverts it into Everitt's salt with formation of red prussiate. Williamson's blue forms after drying a magnificent violet-blue powder, insoluble in water and in dilute acids. A suspension of it in water appears green in transmitted light.

2. *Ferri-cyanide (of potassium) and ferric salt* solutions, when mixed together, give an intense brown liquid which is generally supposed to contain ferric ferri-cyanide, which of course is isomeric if not identical with ferric cyanide,  $\text{FeCy}_3$ . On addition of reducing agents the solution becomes blue, and may deposit blue precipitates.

3. *Ferrocyanide and ferric salt, or ferri-cyanide and ferrous salt.* If the iron salt is in excess over the prussiate, either combination leads to the formation of a dark-blue precipitate insoluble in water and in cold mineral acids,

<sup>1</sup> Mr. Frank Lyall, when a student in my laboratory, tried to test the assumption synthetically. i.e. by mixing known quantities of the co-reagents as standard solutions in a tared flask, allowing the precipitate to settle, in the absence of air, and analysing aliquot parts of the decantate. The solutions, before being mixed, were freed from their absorbed air by boiling, but mixed cold, and in all cases an excess of ferrous salt ( $\text{FeSO}_4$ ) was used. The results were in accordance with the assumption.

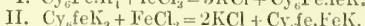
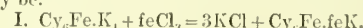
and in both cases the reaction consists in this, that the whole of the potassium of the prussiate is replaced by its equivalent of ferricum or ferrosium respectively. From yellow prussiate we obtain 'Prussian blue'  $\text{Cy}_6\text{FeFe}_2$  or  $\text{Cy}_3\text{Fe}_2\text{Fe}$ . From red prussiate we obtain 'Turnbull's' or rather Gmelin's blue  $\text{Cy}_6\text{FeFe}_2$  or  $\text{Cy}_3\text{Fe}_2\text{Fe}$ . These facts were ascertained long ago by Williamson, and accepted universally as correct, until Reindel threw out the conjecture that ordinary Prussian blue, as prepared from ferrous salt and yellow prussiate, with the help of oxidising agents, might be identical with Turnbull's blue. Reindel's presumption could not reasonably be assumed to hold for Prussian blue properly so called; yet the generally adopted formulae of the two blues stood in need of confirmation, and it was probably this consideration which caused E. J. Reynolds to examine into the matter (C. J. Trans. 1887, 644). He prepared solutions of hydrogen ferrocyanide and ferricyanide, and precipitated them with ferric chloride and ferrous sulphate respectively. The two acids were prepared from the lead salts by means of air-free dilute sulphuric acid; the iron-salt solutions likewise were freed from air before use and the precipitation conducted in an atmosphere of carbonic acid. Both precipitates were dried *in vacuo* over oil of vitriol, and, in the dry substances, the iron and the carbon were determined. The ratios (iron : carbon) found were in perfect accordance with the formula  $\text{Cy}_6\text{Fe}_2\text{Fe}$  and  $\text{Cy}_6\text{Fe}_3$ , respectively. In well-dried samples the percentages of water were in approximate accordance with the formula  $\text{Fe}_2\text{Cy}_6 \cdot 14\text{H}_2\text{O}$ , and  $\text{Fe}_3\text{Cy}_6 \cdot 12\text{H}_2\text{O}$  respectively.

*Prussian blue*, if pressed before being dried, occurs in the shape of compact pieces, which are intensely blue, but, when rubbed against a smooth hard surface, assume a coppery lustre, as indigo does. The compound is proof against the action of cold aqueous acids generally, but very dilute solution of oxalic acid dissolves it largely into an intensely blue liquid, which used to be employed as a blue ink, but which is now superseded by the aniline blues. It is soluble also in solution of ammonium tartrate. If suspended in water and treated with chlorine, it becomes green; the solution contains ferric chloride. The original blue colour is restored on washing with water. Cold concentrated sulphuric acid unites with Prussian blue into a white paste without evolution of gas; on addition of water the original blue is re-generated. Concentrated hydrochloric acid decomposes Prussian blue slowly with formation of ferrocyanic acid, which latter, on the application of heat, suffers its characteristic decomposition (*v. supra*). Aqueous caustic potash and soda decompose Prussian blue very readily with elimination of the extra-radical iron as ferric hydrate and formation of yellow prussiate of alkali. Alkaline carbonates act similarly but less energetically. A tissue dyed with Prussian blue, i.e. the blue substance derived from prussic acid, loses its colour on prolonged exposure to sunlight, but gradually regains it in the dark. In a vacuum Prussian blue is not changed by the light. Dry Prussian blue, if heated in the air, burns like tinder, and leaves an ash containing both oxides of iron.



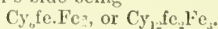
Turnbull's blue resembles Prussian blue, but its colour is lighter, and almost free from eupreous lustre. When heated in air it passes into Prussian blue with elimination of 1Fe in every  $\text{Fe}_3\text{Cy}_{26}$  as oxide. When boiled with caustic potash, it exchanges its ferrosium for potassium, but the red prussiate and ferrous hydrate thus produced at once act upon more caustic potash, so that ultimately potassium ferrocyanide (only) and ferroso-ferrie oxide are produced. This reaction affords a means for detecting an admixture of Turnbull's in Prussian blue.

(4.) *Combinations (3), with excess of Prussiate.* It has long been known that the blue precipitate obtained by adding ferric salt to an excess of prussiate is not Prussian blue, but differs from it by being soluble in pure water, though insoluble in the salt solutions within which it is produced. Reindel was the first to ascertain the correct composition of this 'soluble Prussian blue' as it used to be called, and Seraph subsequently showed that the blue precipitate obtained from ferrous salts by addition of excess of red prussiate is identical with the one derived from ferric salt and ferrocyanide, and that the soluble blue behaves towards iron salts as explained below. The reaction between ferric salt and yellow prussiate, and that between ferrous salt and red prussiate, consist both in this, that in every molecule ( $\text{Cy}_6$  &c.) of prussiate an equivalent quantity of potassium is replaced by an atom of ferrium or ferrosium as the case may be.

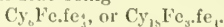


The products, from their formulæ and origin, would appear to be only isomeric, one being a ferrocyanide of ferrium and potassium, the other a ferriecyanide of ferrosium and potassium; but experience shows that they are identical, and that both are entirely different from Williamson's blue, although they agree with it in elementary composition. If soluble Prussian blue is digested with either kind of iron chloride, the potassium goes out, and its place is taken by an equivalent of ferrosium or ferrium as the case may be. In the former case the ultimate product is Turnbull's blue, in the latter it is Prussian blue.

Turnbull's blue being



Prussian blue being



It is worth while to note in passing that either blue can be produced from yellow or from red prussiate.

*Commercial blues.* The practical colour-maker, as a rule, does not aim at the production of any particular ferro-ferriecyanide; all he cares for is to produce a good pigment at the lowest possible price. On account of the latter consideration Turnbull's blue nowadays is hardly ever produced expressly; it comes in only as a by-product in the manufacture of red prussiate, being the best thing to make out of the mother-liquors. According to J. G. Gentele<sup>1</sup> the best blues are obtained by precipitating, in the first instance, ferrous salt with yellow prussiate, and

then oxidising the precipitate. For the manufacture of '*Paris blue*' (meaning the best quality of ferro-cyanogen blue), Gentele gives the following directions:—50 kilograms of yellow prussiate are dissolved in 250 kilos. of boiling water. On the other hand, 45 to 42.5 kilos. of pure green vitriol are dissolved in about the same quantity of water, preferably in the presence of scrap-iron to prevent formation of ferric salt. After the solutions have cleared they are run simultaneously into 250 kilos. of water contained in a tank large enough to accommodate the whole. The whole precipitate produced is allowed to settle for a night, and then collected on a cloth filter. It should form a smooth, greasy, not a granular paste, and be substantially white; the formation of a blue skin can, of course, not be prevented. As soon as the precipitate has drained sufficiently to be taken off the cloth by means of a spatula, it is ready for the operation of '*blueing*,' which can be carried out in a variety of ways. The oldest method is to heat the paste in a basin to boiling, to transfer it, while still hot, to a wooden tub, and then to add, for 50 kilos. of yellow prussiate used, 25.5 kilos. of nitric acid, of 27° Beaumé, and 18 kilos. of sulphuric acid of 66° Beaumé. The order in which the two acids are added is of no consequence. This operation in general involves the evolution of abundance of nitrous fumes, but while in some cases these fumes come off at once, in others they make their appearance only after several hours' standing. In the presence of an excess of green vitriol the fumes always come off at once. 'A precipitate not produced with excess of green vitriol does not effervesce with the acids, and never gives a fiery blue.' After addition of the acids, the whole is left to itself for 24 hours, and the mass is then transferred to a larger tank containing water, with which it is mixed and allowed to settle. The precipitate is washed thoroughly by decantation with cold water, i.e. until the last washings give only a faint turbidity with barium chloride; the more completely the precipitate is washed, the better its colour after drying. The washed precipitate is collected on linen filters, in which it is being pressed so as to produce thin cakes, which are cut up into cubes. These are allowed to dry in the air, and then dried more completely in a chamber at 30° to 40°. The more sharply the cubes are dried the better their lustre, which is eupreous. From the quantities of materials given 39 to 39.5 kilos. of finished blue are obtained.

Another mode of '*blueing*' is to add solution of ferric chloride instead of the acids named. The mode of operating is exactly the same, including the preliminary heating of the paste in a basin. The addition of ferric solution is continued until the application of reagents shows that the liquid contains unchanged ferric in addition to ferrous salts.

Of other oxidising agents available for the oxidation of the white ferrous ferrocyanide, chlorine, according to Gentele, is one of the best. He prefers to use the chlorine as such. The white paste is transferred to a wooden tank and diluted with water and a few pounds of hydrochloric acid to render it more fluid. Chlorine gas is then passed into the mass as fast as

<sup>1</sup> Lehrbuch der Farbenfabrikation, 2nd edition, 1880 (Braunschweig, Vieweg & Sohn).

the apparatus will yield it. The chlorination is continued until a sample of the filtered liquid, when mixed with yellow prussiate, gives a distinctly blue, or no longer a pale-blue precipitate. The fully chlorinated precipitate is washed with water by decantation as usual.

Some manufacturers use hydrochloric together with nitric acid, or bleaching-powder along with hydrochloric acid; but these methods, according to Gentele, offer no real advantage over the one in which chlorine gas is used. Of all the oxidising agents named, chlorine, according to Gentele, is the cheapest; but it is least popular with colour-makers because it involves the setting up of a chlorine evolution apparatus.

From these descriptions it appears clear that 'Paris blue' is in general a mixture of what we called 'Prussian blue,' Turnbull's blue, and Williamson's blue, and, possibly, other cyanides of iron. The pigment which in (German) *commerce* goes by the name of 'Prussian blue,' is 'Paris blue' mixed with starch, heavy spar, gypsum, burned and finely ground kaoline, or other diluents. The white admixture, after having been ground very finely by itself, is added to the Paris blue paste, and along with it passed through a colour-mill repeatedly until no white points are visible in a sample after drying. Very low qualities of blue are often 'faced.' This is done by making the dried cubes rotate in a cask, charged with fine dust of pure Paris blue.

**Thiocyanates, or Rhodanides, or Sulphocyanides.** For the making of thiocyanates in the laboratory yellow prussiate of potash generally serves as the starting-point. From it

The *potassium salt*  $\text{NCS.K}$  is easily produced by the following process due to Liebig. An intimate mixture of 46 parts of perfectly anhydrous prussiate of potash, 17 of recently ignited potassium carbonate, and 32 of sulphur is fused in an iron crucible until the evolution of gas ceases, and the fused mass is then poured out into an iron tray. The mass is powdered coarsely, and either boiled out directly with alcohol and the salt allowed to crystallise out of the filtered solution on cooling, or else the mass is first lixiviated with water, an impure salt made to crystallise out, and this then purified by recrystallisation from alcohol. Henneberg prefers to first produce a *hepar* from the potassium carbonate and the sulphur, and only then to add the prussiate.

*Potassium thiocyanate* crystallises, more readily from alcoholic than aqueous solutions, in long striated prisms or needles, fusing at  $161.2^\circ$  (Pott), sp.gr. = 1.886 to 1.906 (Bödecker). Its aspect and taste are similar to those of salt-petre. The crystals are anhydrous and deliquesce in the air. 100 parts of water at  $0^\circ$  dissolve 177.2; at  $20^\circ$ , 217.0 parts of the salt, with very considerable absorption of heat. According to Vogel the salt is a narcotic poison.

*Ammonium thiocyanate*  $\text{NCS.NH}_4$  may be prepared from the potassium salt in a manner analogous to that which serves for the production of urea from potassium cyanate, *i.e.*, by mixing strong solutions of potassium thiocyanate and ammonium sulphate (in equivalent proportions), allowing the potassium sulphate to crys-

tallise out, evaporating to dryness over a water-bath, and extracting the ammonium thiocyanate with alcohol. Liebig recommends to prepare the salt by digesting ammonium cyanide solution with one of yellow ammonium sulphide.

*Ammonium thiocyanate* forms colourless leaflets which are easily soluble in water and in alcohol. 100 parts of water dissolve 122 parts of the salt at  $0^\circ$ , and 162 parts at  $20^\circ$ . If 133 parts of the salt be dissolved in 100 of water at  $13^\circ$ , the temperature falls to  $-10^\circ$  (Rüdorf); sp.gr. = 1.3075 at  $13^\circ$  (Clarke). Dry ammonium thiocyanate fuses at  $159^\circ$  (Reynolds); if kept at this temperature, it suffers progressive conversion into its isomer thio-urea. If kept at  $190^\circ$  for twenty hours, the thio-urea loses  $\text{H}_2\text{S}$  and becomes cyanamid  $\text{NC.NH}_2$ , which unites with  $\text{NCS.NH}_4$  into hydro-thiocyanate of guanidine  $\text{CHN}(\text{NH}_2)_2.\text{CNSH}$ .

Ammonium thiocyanate is used in the laboratory as a test for ferric iron, and as a precipitant for silver (Volhard's method of silver-titration).

The methods which we gave above for the preparation of the salt have now only an historical interest, because thiocyanate of ammonium has come to be made industrially by means of that method of Gélis which we have had occasion to refer to before, and of which we stated that it had been brought into more workable forms by Günzburg and Tcherniac.

#### MANUFACTURE OF THIOCYANATES ACCORDING TO GÉLIS' METHOD, AS MODIFIED BY GÜNZBURG AND TCHERNIAC.

*Requisites.*—(1) A pump made entirely of iron, as used for the production of cold by means of ammonia (B in fig. 4).

(2) A series of autoclaves of wrought-iron tested for high pressure. Each autoclave is provided with an agitator with paddles, a manometer, a thermometer, and three stopcocks: one for letting in the liquid from the pump, another for letting off the gases, and a third for discharging the contents. The autoclaves are surrounded by steam jackets; they communicate, each by a system of pipes, with the feeding pump and the still. In the manometers, those parts which are in contact with the gases must be made of iron or of platinum, they must each of them be provided with a tube which dips into the liquid, or else they soon cease to give correct readings through ammonium sulphide subliming on the membrane or curved hollow tube.

(3) A still, heated by means of a close spiral steam-pipe. The still is surmounted by a cylindrical vessel called the 'dévaseur,' the object of which is to catch the spray, so that only vapour and gases can travel on through F and G into the reservoir H, where the liquid distillate accumulates. F is a coke-tower, G a refrigerator; a pump serves to constantly pour liquid over the coke in F, and let it trickle over it and rain through G into H.

(4) A gas-holder, L, of about 15 cubic metres capacity, into which the uncondensed gases pass from H.

All the apparatus described so far is made of iron, except the spiral pipe of the still, which consists of block tin, or else the ammonium thiocyanate solution in the still, as soon as it

ceases to be strongly alkaline, gets contaminated with iron. But to obtain solutions which are perfectly free from iron aluminium must be used.

*Method of working.*—By means of a feeding pump the autoclaves are charged with carbon di-sulphide, ammonia of 20 p.c., and a certain proportion of aqueous distillates recovered from previous operations. As soon as an autoclave has received its charge, the inlet-stopcock is closed, the agitator set in motion, and the steam turned on and allowed to act, until the thermometer of the autoclave marks 100°; the steam

is then stopped, but the agitator kept going, until the manometer indicates a pressure of 15 atmospheres; the reaction is now at an end, and the liquid is ready to be blown over into the still.

In the still the liquid, which is a solution of ammonium thiocarbamate mixed with un-attacked carbon disulphide, is heated to 105–110° to cause the thiocarbamate to break up into sulphuretted hydrogen and ammonium thiocyanate, which latter remains in the still in aqueous solution: the volatile products make

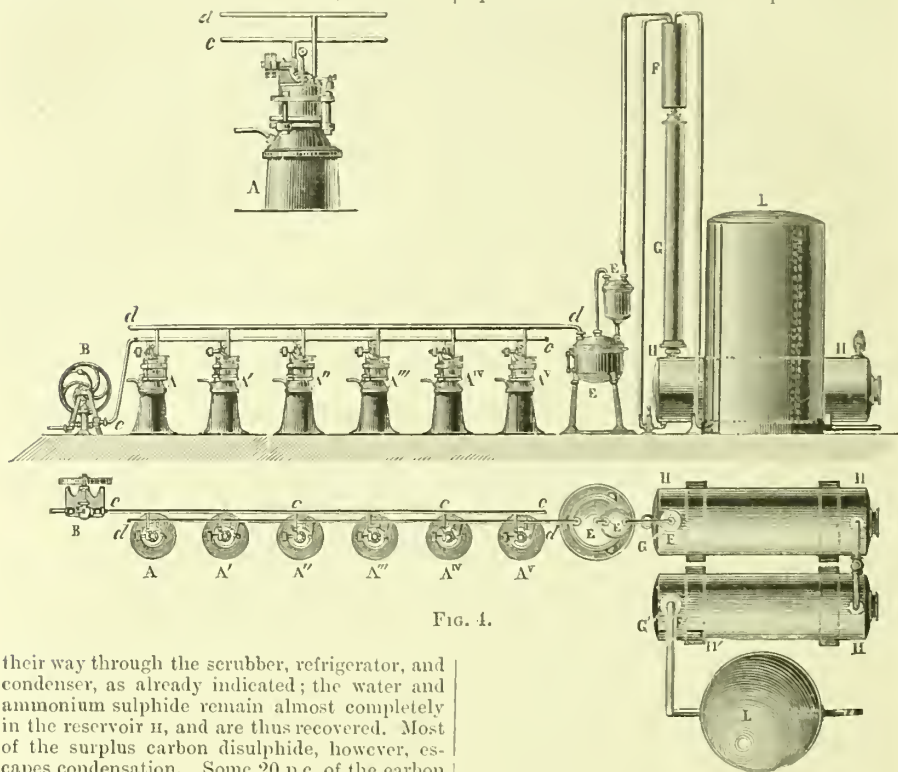


Fig. 4.

their way through the scrubber, refrigerator, and condenser, as already indicated; the water and ammonium sulphide remain almost completely in the reservoir *u*, and are thus recovered. Most of the surplus carbon disulphide, however, escapes condensation. Some 20 p.c. of the carbon disulphide used to be thus lost, until it was found that its vapour can be separated very completely from the gases by scrubbing these with oil. Any kind of fatty oil will do; but heavy petroleum is the cheapest absorbent. Since the introduction of this improvement the yield of ammonium thiocyanate has been brought up to 95 p.c. of the theoretical amount.

To obtain crystallised ammonium thiocyanate the solution remaining in the still is evaporated at 125° and allowed to stand in wooden tanks lined with tin. If the salt contains ever so little iron, it becomes red in the air and unsaleable; but the iron can easily be removed from the solution by means of ammonium sulphide, or by ammonium hydrate in the presence of air. The filtrate must be evaporated in a tin basin.

**Calcium thiocyanate.** For the conversion of the ammonium into calcium salt, the apparatus represented in fig. 5 is used. It consists of a cylindrical upright still *A*, heated by means of a worm, and inclosing a perforated sheet-iron

cylinder for the lime. The still is provided with a thermometer and a discharge-cock; it communicates (1) with a froth-eatcher, *E*; and (2) through it, with a refrigerator *u*, terminating in a receiver, kept cool by a worm through which cold water is made to circulate.

The ammonium thiocyanate solution having been introduced into the still, and the basket been charged with lime, the apparatus is closed, and the temperature raised quickly to 125°. The ammonia distils over as an aqueous solution of about 20 p.c., which is utilised in the synthetical process, while the still, at the end of the operation, contains a solution of calcium thiocyanate.

**Potassium thiocyanate.** This salt is prepared from the calcium salt by double decomposition with potassium sulphate. The operation is carried out in open cylindrical iron pots, which are heated over a naked fire, and are provided with agitators. A boiling concentrated solution



of a little more than the calculated quantity of potassium sulphate is first prepared, and the calcium salt is then added in instalments with agitation, the mixture being kept at a boiling heat. The calcium sulphate separates out quickly on standing; it is separated from the liquor by means of a filter-press. A small quantity of lime which the liquor retains is removed by pre-

case of sodium carbonate. In the ordinary process for the recovery of the sodium carbonate the cyanides pass into the ultimate mother-liquor, along with caustic soda, sodium sulphide, &c. Unfortunately we know of no process for eliminating the cyanogen in any useful form, which would not involve the destruction of the caustic soda. It pays better to destroy the cyanide and save the caustic alkali.

**Manufacture of coal-gas.**—As a matter of experience the tar-water produced in the distillation of coal invariably contains a small quantity of ammonium thiocyanate; and, if Laming's mass be used for the purification of the gas, this mass gradually gathers cyanogen, partly in the form of thiocyanate. There is no difficulty in accounting for its formation. The vapour which issues from the retort contains ammonia and carbon disulphide. The ammonia, being in contact with red-hot carbon, yields ammonium cyanide, part of which remains in the tar-water, while the rest goes to the Laming purifiers, to be converted, part into calcium cyanide, part into thiocyanate, by combination with the sulphur which abounds there. The thiocyanate of the gas-water is produced by the interaction of carbon disulphide, ammonia and water.

The tar-water is used for the manufacture of ammonium sulphate, by distilling it either alone or after addition of lime, and passing the vapours into an excess of chamber-acid (*v. AMMONIA*). In the former case, if there is any ammonium cyanide, its hydrocyanic acid passes into the ammonium sulphate liquors and is lost; in the latter it remains in the residue as calcium salt. The thiocyanogen in either case remains in the residue, as ammonium salt or calcium salt respectively.

A great number of patents have been taken out for the conversion of the cyanogen of these compounds into commercially valuable products (*Bib. 44-48*). Of these schemes, that of Gauthier-Bouchard appears to us the most plausible; a number of the later proposals, indeed, are little more than modifications of it.

The Paris gas company purify their gas by passing it over a mixture of ferric hydrate and calcium sulphate, obtained by mixing lime and green vitriol and exposing the mixture to the air. A certain proportion of saw-dust is incorporated with the mixture in order to render it more porous. The ferric hydrate absorbs the sulphuretted hydrogen, while the calcium sulphate fixes the ammonia. The ammonium sulphate is extracted with water; the residue left serves as the raw material for the Gauthier-Bouchard process. The first step is a preliminary treatment with water, which extracts some iron thiocyanate. This may be turned into ammonium salt and thence into prussiate, by means of the process of Gélis. The residues are mixed with lime, 30 kilos of lime for every cubic metre (or about 1,600 kilos) of lixiviated mass, and the whole is subjected to a systematic lixiviation with water. The residue is allowed to weather for 3 to 4 months, and then again lixiviated. The liquors obtained contain calcium ferrocyanide, a little thiocyanate, and ammonia salts. The more concentrated liquors are evaporated to obtain crystals of calcium

FIG. 5.

cipitation with potassium carbonate. The filtered solution is evaporated at 125° and allowed to cool; it deposits the whole of its sulphate and chloride, so that nothing but pure thiocyanate remains in solution. The solution is evaporated to dryness, and the dry salt fused at 300° in an iron basin, to be ready for conversion into prussiate by the process which we have already described (*v. supra*, p. 633).

#### CYANIDES AS BY-PRODUCTS.

Notable quantities of cyanides are produced incidentally in the following industries:—

**The Leblanc process.**—In the black-ash process the necessary carbon is always used in the form of coal, and as all coal contains nitrogen, the product is bound to contain alkaline cyanide, which, in the process of lixiviation, is sure to assume the form of prussiate, because there is always more than enough of that alkaliferous iron sulphide which, in the prussiate process, effects this conversion. The proportion of cyanogen in black ash is, of course, subject to considerable variation. According to Nietzki, there are about 12 parts of alkaline prussiate and 6 of rhodanide in the liquor produced from 10,000 parts of black ash. Nietzki's figures refer to the

ferrocyanide, which is converted into potassium salt. The weaker solutions are worked up for an inferior quality of Prussian blue. This process is being wrought at d'Aubervilliers.

The great difficulty in connection with this matter, obviously, is the economic conversion of thiocyanate into prussiate, or cyanide. According to A. Sternberg (Bib. 49), soluble thiocyanates can be de-sulphurised in the wet way, provided that the conditions for the formation of prussiate are established. He mixes the solution of the rhodanide with twice the calculated quantities of iron filings and of recently precipitated ferrous hydrate, and heats the mixture to 110° to 120° in an autoclave provided with an agitator. The more concentrated the rhodanide solution, the quicker the change. After about 12 hours some 80 p.c. of the rhodanide is reduced. (For further information see the source quoted.)

It might be possible to utilise Erlenmeyer's process of oxidation for the conversion of thiocyanates into cyanides. Erlenmeyer's permanganate, it is true, would be too expensive, but presumably manganese dioxide and sulphuric acid would work as well. From the mixture containing sulphuric and hydrocyanic acids, the latter might be distilled into caustic potash ley, holding ferrous hydrate in suspension, and thus be converted into prussiate.

Storek and Strobel (Bib. 48a) propose to work up gas-water thiocyanate by precipitating the NCS as cuprous salt, washing the precipitate and next decomposing it with baryta-solution to obtain barium thiocyanate, which serves as a starting-point for the preparation of other thiocyanates.

*The process of iron smelting*, as already remarked above, involves the formation of large quantities of potassium cyanide which might be recovered (comp. *supra*, p. 632).

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*Recovery of cyanides from Leblanc residues or gas-water, &c.*

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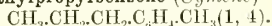
W. D.

**CYANINE** v. QUINOLINE COLOURING MATTERS.

**CYANOSINE** v. TRIPHENYLMETHANE COLOURING MATTERS.

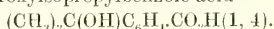
**CYMENES.** *Cymols.* The name *cymene* was first applied to the hydrocarbon (*p*-methylpropylbenzene) isolated by Gerhardt and Cahours (A. Ch. [3] 1, 102 and 372) from Roman oil of cumin, which is the ethereal oil of *Cuminum cyminum*. Frequently, however, the various benzene hydrocarbons of the formula  $C_{10}H_{14}$  are grouped together under the collective name of *cymenes*. No fewer than 22 of these are theoretically possible, of which more than half have been prepared; but only the most important, namely, *cymene* proper (*p*-methylpropylbenzene) and the tetramethylbenzenes, can be described here.

*p*-Methylpropylbenzene (*Cymene*)

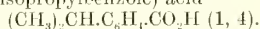


Occurs in Roman oil of cumin (Gerhardt and Cahours, *l.c.*); in the volatile oil from the seeds of the water-hemlock (*Cicuta virosa*) (Trapp, A. 108, 386); in the oil from *Ptychotis ajowan* (H. Müller, B. 2, 130); in oil of thyme (Lallemand, A. 102, 119) along with thymol  $C_{10}H_{14}O$  and thymene  $C_{10}H_{16}$ ; and in eucalyptus oil (from *Eucalyptus globulus*) (Faust and Homeyer, B. 7, 1429). May be obtained from camphor by abstracting from it the elements of water  $C_{10}H_{16}O = C_{10}H_{14} + H_2O$  by heating it either with phosphorus pentoxide (Dumas, A. Ch. 50, 226; Delalande, A. Ch. [3] 1, 368) or with phosphorus pentasulphide (Pott, B. 2, 121) or with phosphorus pentachloride (Lippmann and Louguinine, Bl. [2] 7, 374). Various isomerides of camphor yield *cymene* by the same treatment. The terpenes  $C_{10}H_{16}$  may be converted into *cymene* by withdrawing two atoms of hydrogen: this may be effected in the case of oil of turpentine, for example, by distilling it with bromine (Oppenheim, B. 5, 94 and 628), or better, with iodine (Kekulé, B. 6, 437). Old turpentine generally contains *cymene*. It has been obtained synthetically by the action of sodium on a mixture of *p*-bromotoluene and

normal propyl bromide (Fittig, Schäffer and König, A. 149, 334). To prepare *cymene*, camphor is warmed with an equal weight of phosphorus pentoxide, the *cymene* is poured off, treated again twice with a little phosphorus pentoxide, and finally rectified from sodium. The yield varies from 50 to 80 p.c. (Fittica, A. 172, 307).—Liquid boiling at  $175.4-175.5^\circ$  under 749.5 mm.; sp.gr.  $0.864^{98}_4$  (R. Schiff, A. 220, 94). With chromic acid it yields terephthalic acid  $C_6H_4(CO_2H)_2 (1, 4)$ ; with potassium permanganate hydroxyisopropylbenzoic acid



Taken internally it reappears in the urine as cumic (*p*-isopropylbenzoic) acid



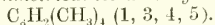
In both these last cases the normal propyl group is transformed into the isopropyl group. This change and the reverse change of isopropyl into propyl are very common with the para-*cymene* derivatives, and have greatly added to the difficulty of ascertaining the constitution of these compounds. The rule is that, when the methyl group in the para-position to the propyl group is converted into  $CH_2OH$  or  $CHO$  or  $CO_2H$ , the propyl group changes into the isopropyl group, whilst on re-generating methyl from these oxygenated groups the isopropyl group changes back into the propyl group (cf. Widman, B. 19, 254).

#### Tetramethylbenzenes:

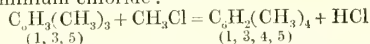
1. *Consecutive tetramethylbenzene* (*Prehnitene*)  $C_6H_2(CH_3)_4 (1, 2, 3, 4)$ . When sodium durene-sulphonate

$C_6H_2(CH_3)_3SO_3Na$  ( $CH_3$ -groups 1, 2, 4, 5, v. *infra*) is dissolved in concentrated sulphuric acid and allowed to stand for twelve hours, prehnitene-sulphonic acid is formed. The mixture is diluted with water, saturated with barium carbonate, the barium salts converted into sodium salts, and these, by treatment with phosphorus pentachloride and ammonia, transformed first into sulphonic chlorides and then into sulphonamides. Prehnitenesulphonamide is separated by means of its sparing solubility in alcohol, and is then hydrolysed by heating with concentrated hydrochloric acid to  $170^\circ$ , when it yields prehnitene (Jacobsen, B. 19, 1213). Also obtained by heating bromocumene  $C_6H_4Br(CH_3)_3$  ( $CH_3$ , Br,  $CH_3$ ,  $CH_3$ : 1, 2, 3, 4) with methyl iodide, benzene, and sodium, in a sealed tube at  $150^\circ$  for twelve hours.—Liquid boiling at  $204^\circ$  (cor.). Solidifies in a freezing mixture and melts at  $-4^\circ$ . Dilute nitric acid oxidises it to prehnitic acid  $C_6H_2(CH_3)_4CO_2H$ .

#### 2. *Unsymmetrical tetramethylbenzene*



From bromomesitylene (v. CUMENES), methyl iodide and sodium in presence of benzene (Jannasch, B. 8, 356). Best by passing methyl chloride into a mixture of mesitylene and aluminium chloride:



(Jacobsen, B. 14, 2629).—Liquid boiling at  $195-197^\circ$ . Solidifies in a freezing mixture. With dilute nitric acid it yields three isomeric acids of the formula  $C_6H_2(CH_3)_4CO_2H$ ; potassium permanganate ultimately converts it into mellophanic acid  $C_6H_2(CO_2H)_4 (1, 3, 4, 5)$ .



*Symmetrical tetramethylbenzene (Durene)*  $C_6H_2(CH_3)_4$  (1, 2, 4, 5). Occurs in coal-tar (Schulze, B. 18, 3032). By the action of sodium on a mixture of bromopseudocumene  $C_6H_2(CH_3)_2Br$  (1, 2, 4, 5), methyl iodide and sodium (Jannasch and Fittig, Z. 1870, 161). From toluene and methyl chloride in presence of aluminium chloride (Friedel and Crafts, A. Ch. [6] 1, 461). Best from *o*- or *p*-xylene, methyl chloride and aluminium chloride (Jacobsen, B. 14, 2629).—Crystalline mass,

smelling like camphor.—Melts at 79-80 and boils at 189-191 (Jacobsen). Yields by oxidation with potassium permanganate finally pyromellitic acid  $C_4H_2(CO_2H)_4$  (1, 2, 4, 5).

F. R. J.

CYMOLS *v.* CYMENES.CYMOPHENOL *v.* CAMPHORS.CYPRIAN VITRIOL. *Copper sulphate v. COPPER.*CYTISINE *v.* VEGETO-ALKALOIDS.

## D

DAGUERRETYPE *v.* PHOTOGRAPHY.DAHLIA. *Syn. Hofmann's violet, Primula v. TRIPHENYLMETHANE COLOURING MATTERS.*DAMMARA RESIN *v.* RESINS.DAMMARAN *v.* RESINS.DAMMARIC ACID *v.* RESINS.DAMMAROL *v.* RESINS.DAMMARONE *v.* RESINS.DAMMARYL *v.* RESINS.

DANDELION ROOT. *Taraxaci Radix*. (*Pissenlit*, Fr.; *Löwenzahnwurzel*, Ger.) The root of the common dandelion, *Taraxacum officinale* (Wiggers; Benth. a. T. 159), is used in medicine for its mild laxative and tonic properties. It is administered either in the form of expressed juice or weak spirituous extract. The roots employed should be collected in the autumn. For a summary of the earlier chemical examinations of the root, see Pereira (Mat. Med. 1853 [2] 1574). According to Kromayer (Ar. Ph. 105, 6) there separates from the milky juice on standing a coagulum, 'leontodonium,' from which hot water dissolves a bitter substance. The bitter compound is removed from the solution by animal charcoal, from which it is extracted by alcohol, and after further purification constitutes the *taraxacin* of Kromayer. A similar *taraxacin* in warty crystals had been previously described by Polex (Ar. Ph. 19, 50). From that part of the coagulum left undissolved by the water alcohol extracts crystalline *taraxacrin*  $C_8H_{16}O$  (Kromayer).

Among the other constituents of the root are *inulin* (Frückinger, R. P. 23, 45, Widemann, R. P. 43, 281; Overbeck, Ar. Ph. 23, 240) and *levulin* (Dragendorff, Sachsse's Farbstoffe, 125). Mannite, which had been often found in the juice, was shown by T. a. H. Smith not to pre-exist in the root but to be a product of fermentation (Ph. 8, 480). In the root collected in October Dragendorff found 24 p.c. of inulin, while that collected in March contained only 1.7 p.c., associated, however, with 17 p.c. of uncrystallisable sugar and 19 p.c. of levulin. From the last mentioned compound is an isomeride of inulin, being distinguished by its solubility in cold water, the sweetness of the solution, and by the absence of any action on polarised light.

The leaves and stalks, but not the root of the dandelion, contain *inosite* (Marmé, A. 129, 222).

A. S.

DAPHNETIN *v.* RESINS.DAPHNIN *v.* GLUCOSIDES; also RESINS.DAPICHO or ZASPIS. The South American name for the caoutchouc which exudes from the roots of *Siphonia elastica*.DARWINITE *v.* DOMEYKITE.DATHOLITE *v.* DATOLITE.

DATISCA CANNABINA. *Bastard hemp*. A plant found in Southern Europe and in India, the leaves of which are used for dyeing silk. The colouring matter, *datisca* yellow, is a pale yellow-brown translucent mass, soluble in water and giving a permanent yellow to cotton mordanted with alum. The roots of the plant contain a colourless glucoside, *datisein*  $C_{21}H_{42}O_{12}$ , crystallising in silky needles, melting at 180°, and yielding by hydrolysis *datiscetin* and glucose  $C_{21}H_{42}O_{12} = C_{15}H_{30}O_8 + C_6H_{12}O_6$ .  
*Datisein      Daticetin      Gluco c.*

*Daticetin* forms colourless needles, almost insoluble in water but readily soluble in alcohol and ether (Stenhouse, A. 98, 166).

DATOLITE. A native boro-silicate of calcium, discovered near Arendal, in Norway, by Esmark in 1806. It derives its name from *δατέομαι*, 'to divide,' in allusion to its readily breaking with a granular fracture; Werner, however, incorrectly spelt it *Datholite*, whence it has been supposed that the name is connected with *δαδρος*, 'turbid,' though the best-marked varieties are remarkable for their transparent vitreous character. The mineral crystallises in the monoclinic system, but occurs also massive, and a variety from Lake Superior, of opaque white colour, is so compact as to resemble unglazed porcelain.  $H. = 5$  to  $5.5$ ; sp.gr.  $2.8$  to  $3.4$ .

Datolite was originally analysed by Klaproth, and the boric acid was first determined directly by Stromeyer. The following are modern analyses of typical varieties:—

	I.	II.	III.	IV.
SiO <sub>2</sub>	35.74	38.48	26.21	36.99
B <sub>2</sub> O <sub>3</sub>	22.60	20.31	22.61	20.10
CaO	35.11	35.64	35.14	33.35
H <sub>2</sub> O	6.14	5.57	5.81	5.87

I. From Bergen Hill, New Jersey (Whitfield). II. From Andreasberg (Rammelsberg). III. From Baveno (Molinari). IV. From Kugelbad (Preis).

Datolite is occasionally found in the trap-rocks of Scotland, especially in the Kilpatrick

Hills. The finest crystals are found at Bergen Hill, N. Jersey, and have been studied by E. S. Dana (Am. S. [3] 4, 16).

It occurs in veins of silver ore at Andreasberg, in the Hartz; in granite at Baveno, near Lago Maggiore; in serpentine at Monte Catini in Tuscany; and in amygdaloidal melaphyre at Theiss in Tyrol, and many other localities. A botryoidal variety, from Arendal in Norway, containing as much as 8.6 p.c. of water, is distinguished as *Botryolite*. At Haytor, in Devonshire, a rare pseudomorph was formerly found consisting of large crystals of datolite completely replaced by quartz: this mineral is known as *Haytorite*. (For an exhaustive description of datolite, with bibliography, v. O. Lüdecke, Ueber Datolith: eine mineralogische Monograph, Zeitschr. f. Naturwiss. Halle [4] 7, 1888, 235-403).

F. W. R.

**DATURA STRAMONIUM.** *Thorn-apple.* (*Stramoine*, Fr.; *Stechapfel*, Ger.) The seeds and leaves of *Datura Stramonium* (Linn.) are employed in medicine for their sedative and narcotic properties. The former are administered in the form of tincture or solid alcoholic extract, and the latter are smoked as a remedy for asthma. According to De Candolle the plant is indigenous to the neighbourhood of the Caspian Sea, whence it has spread throughout the temperate and warmer parts of the world. (Fl. a. H. 2nd ed. 459; Bentl. a. T. 192).

Like other drugs derived from the *Solanaceæ*, the physiological action of datura depends upon the presence of poisonous alkaloidal constituents. What appeared to be a single alkaloid, 'daturine,' was isolated by Geyer (A. 7, 272). Von Planta (A. 74, 246, a. 252) and subsequently Ladenburg (A. 206, 279) and Schmidt (A. 208, 196; Ar. Ph. 22, 329) have, however, proved that 'daturine' is a mixture of *hyoscyamine*, the alkaloid of henbane, and its isomeride *atropine*, originally obtained from belladonna. In belladonna atropine was supposed to exist together with hyoscyamine, but it has been observed that in the extraction of the alkaloids, the relative proportion of the one to the other depends upon the mode of working. With greater care the yield of hyoscyamine is increased, and that of atropine diminished, and it is possible to obtain the whole of the alkaloid as hyoscyamine. This fact has been investigated by W. Will (B. 21, 1719) who finds that hyoscyamine may be easily converted into atropine by the action of alcoholic solutions of alkalis or by heat alone. It is probable, therefore, that in belladonna, and possibly also in datura, hyoscyamine only is present in the plant, and that it is converted more or less into atropine during the process of extraction (cf. Schmidt, B. 21, 1829; Will a. Bredig, B. 21, 2777). Ladenburg, however, questions this view (B. 21, 3065). Datura leaves contain .02 p.c. of alkaloid, and leave 17 p.c. of ash when burned. The seeds yield about .1 p.c. of alkaloid and a quarter of their weight of a bland fixed oil.

Other species of datura which probably depend for their activity on the same alkaloids are *D. Tatula* (Linn.), *D. alba* (Nees), and *D. fastuosa* (Linn.).

A. S.

**DATURINE** v. *DATURA*.

**DEAD DIPPING.** The process of producing a pale yellow dead surface on ornamental brass-

work. The brass-work, after the final stamping with its adhering black scale from the annealing oven is placed in dilute nitric acid until the scale is detached, when it is removed and washed with water. It is next plunged into stronger nitric acid, and when its surface is covered with minute gas bubbles it is washed in a solution of argol and dried in hot sawdust.

**DEAD OIL.** The higher boiling fractions of shale-oil from which the greater portion of the solid paraffin has been crystallised out.

**DECATOIC ACIDS** v. *FATTY ACIDS*.

**DECHENITE** v. *VANADIUM*.

**DECIPIUM** v. *CERIUM METALS*.

**DECOIC ACID** v. *Capric acid*, art. *FATTY ACIDS*.

**DELTAPURPURIN** v. *AZO-COLOURING MATTERS*.

**DELPHININE** v. *VEGETO-ALKALOIDS*.

**DEPHLEGMATOR.** an apparatus used in distilleries for freeing alcohol from water (*phlegma*).

**DESCLOIZITE** v. *VANADIUM*.

**DEXTRAN** v. *GUMS*.

**DEXTRIN**  $n(C_6H_{10}O_5)_n$ . The use of this term should be now confined to the body obtained by the action of diastase on starch-paste, the preparation of which we shall describe below, and to those substances from other sources which agree in chemical and physical properties with this body.

The substances known in England as dextrin or dextrine, British gum, starch gum, &c.; in France, as amidon grillé, gomme d'Alsace, leigomme, gommeline, &c.; and, in Germany, as dextrin, Stärkekugummi, Rostgummi, &c., obtained by the action of heat, acids, or diastase on starch are not simple bodies, but mixtures, one of the constituents of which may be dextrin, but at present we have little or no evidence of its presence in any of these products. There can be no doubt, however, that they contain, besides sugars (copper oxide reducing substances), bodies closely related to dextrin.

*Occurrence.*—The sap of plants is said to contain dextrin, and it figures in the published analyses of most of the cereals and many other seeds; but its presence, in the majority of cases, requires confirmation. The body isolated by Limpricht (J. 1865, 673) from horse-flesh, probably contains dextrin, but the optical activity, as given by him, is too low for pure dextrin. Reichardt (Ar. Ph. [3] 5, 502) found it in the urine of diabetic patients; this, too, is a doubtful source. It is found in beer, and probably in bread. Braconnot (A. Ch. 12, 172) tried to convert cellulose into dextrin. We have no evidence that either he, or those who followed him—Vogel, Berthelot, or Anthon—were successful; in fact, we know little of the nature of this product. According to Musculus (Bl. [2] 18, 66; C. R. 92, 528), sulphoglucoic acid is converted into dextrin by the action of strong alcohol. Glycogen yields by the action of nitric acid, in the presence of sulphuric acid, dinitro-glycogen, which, upon reduction with ammonium sulphide, yields dextrin  $[\alpha_D] = 194$  (Lustgarten, M. Chem. 2, 626). Hydrochloric acid, sp.gr. 1.026, converts dextrose into a kind of dextrin (Grimaux and Lefèvre, C. R. 103, 146).

The commercial products above mentioned are prepared by the action of:

- a. Diastase on gelatinised starch.
- b. Acids on starch in the presence of water at the boiling or higher temperature.
- c. Heat on dried starch.
- d. Heat on acidified dried starch.
- e. Digestion with alkalis also converts starch into dextrin-like bodies.

For the action of diastase on starch *v. Musculus* (Bl. 22, 32); Payen (*J. Chim. Méd.* 9, 572); O'Sullivan (C. J. 1876, 2, 125); Brown and Heron (C. J. 35, 596); Brown and Morris (C. J. 47, 527); and for that of heat and acids, Biot and Persoz (A. Ch. [2] 52, 72); Payen (A. Ch. 55, 225; 61, 372; 65, 225 and 234); Guérin-Varry (A. Ch. 60, 68); Jacquelin (A. Ch. [3] 8, 225); Béchamp (C. R. 51, 256); Anthon (D. P. J. 218, 182; 219, 457); O'Sullivan (C. J. 10, 581).

*Preparation.*—A moderately thick homogeneous starch-paste is heated to 60–63°, and sufficient cold water extract of malt, or solution of freshly prepared diastase, added to yield, on maintaining the temperature at 60–63° for ten minutes, products from the starch having an optical activity  $[\alpha]_D = 176.6^\circ$  or below. The solution is then quickly cooled and filtered, the filtrate boiled and concentrated to a rather thick syrup; this is best done in a vacuum vessel, but the operation can be effected on a water-bath. The syrup contains dextrin, maltose, and the soluble portions of the malt-extract or diastase employed. By repeated treatment with alcohol, maltose, as well as some of the constituents of the malt-extract and diastase, can be eliminated. The remainder of these substances is separated by dissolving the syrup in a little water and adding alcohol, sp.gr. .83, until about one-eighth of it is precipitated. The supernatant liquid then contains pure dextrin, which can be precipitated by the addition of strong alcohol. If the product thus obtained is capable of reducing copper oxide when a portion of it is boiled with Fehling's solution, it contains maltose. This can be completely removed by repeated precipitation with alcohol, or by diluting the syrup with water, heating to boiling, and adding a slight excess of a solution containing in 100 c.c. 10 grams HgCy<sub>2</sub> and 10 grams NaOH. The reduced mercury is allowed to subside, the clear supernatant solution decanted off, carefully neutralised with hydrochloric acid, and evaporated to a syrup. From this sodium chloride, sodium cyanide, and excess of mercury dicyanide can be removed by dialysis, and dextrin precipitated from the concentrated solution by alcohol. We cannot say that treatment with alkaline mercury dicyanide is to be recommended. Dextrin thus purified is obtained in the solid state by dissolving in a little water, evaporating to a syrup, and drying in a vacuum over sulphuric acid. Thus obtained it is a colourless glassy body, which may be rubbed down to a white powder. It is without marked taste, and is odourless. It is neutral, easily soluble in water, but insoluble in strong alcohol. The solution is not coloured by iodine. Heated in solution with dilute mineral, or with some organic acids, it is converted into maltose, and finally into dextrose. Diastase solution slowly converts it into maltose. It is optically active, the apparent activity being  $[\alpha]_D = 222$ ,  $[\alpha]_D = 200.4$  for a solution containing 10 grams dextrin in 100 c.c. and less.

Fehling solution or alkaline solution of mercury dicyanide is not reduced by it. It does not ferment in presence of ordinary beer yeast, but if active diastase is present it yields alcohol readily. A species of mucor converts dextrin into sugar (maltose?), thence into alcohol and other products (Gujon and Dubourg, C. R. 103, 885). Heated to 220–230° dextrin is converted into pyrodextrin (Gélis, A. C. P. 3 52, 388). Treatment with bromine and silver oxide converts dextrin into dextronic acid, the calcium salt of which is  $C_6H_7CaO_6$  (Haberman, B. 5, 167), isomeric with gluconic acid. Lime and baryta form compounds with dextrin, which are insoluble in alcohol. Nitric acid converts it into saccharic acid and, finally oxalic acid. The dextrin prepared by O'Sullivan's method yields sodium and potassium compounds containing  $C_{12}H_{10}O_{10}Na$  and  $C_{12}H_{10}O_{10}K$  (Pfeiffer and Tollens, A. 210, 285 a, 309). Other dextrins besides this one are produced by the action of diastase on starch (*v. Starch*); they have many characters in common with it, but are distinguished from it by the amount of maltose they are capable of yielding when submitted to the action of diastase at 60–63° for a few minutes. One of them,  $\alpha$ -dextrin, or erythrodextrin, gives a reddish-brown colour in solution with iodine, the others give no colouration with iodine. For estimation of dextrin *v. BEER*; SACCHARIMETRY.

The commercial products above mentioned are now chiefly prepared by the action of heat on starch. The starch is first freed as much as possible from combined water by drying in suitable ovens, and then submitted to a temperature of 212–275° in rotating sheet-iron drums. The heat is supplied by hot oil, rape oil being pretty generally used, or by direct fire. When the oil-bath is used the control over the temperature is greatest, and the colour of the product can be varied at will from white to dark-brown. When the drums are heated by direct fire they are made to rotate on slightly inclined axes, the dried starch being fed in at the higher end of the revolving cylinder and the product discharged at the other. Sheet-iron ovens are also used; they are constructed singly or in sets. The heat is supplied by a furnace, the heated air from which is drawn over the top of the ovens. The material is kept continually stirred by flat iron oars. Boxes and trays are also used as converters, and, indeed, one has only to consider the variety and quality of product required, and to remember that the drier the starch and the lower the temperature of conversion, the whiter will be the product, and, further, that different starches yield different products, i.e. behave differently when submitted to the action of heat, to enable him to construct an apparatus that will suit his requirements. It must also be borne in mind that the conversion takes place more slowly at a low temperature. By moistening air-dried starch with dilute nitric acid, and drying at a low temperature, less heat is required to yield a satisfactory product. Payen recommended 1,000 lbs. starch to be moistened with 30 gallons water containing 2 lbs. nitric acid, sp.gr. 1.38, the mixture to be well kneaded, made up into balls, and dried in a hot-air chamber; then powdered, spread on brass trays to the depth of  $1\frac{1}{2}$  to 2 inches, and submitted to



a temperature of from 110–120° in a hot-air oven.

Hydrochloric acid, oxalic acid, and lactic acid, in the form of sour milk or buttermilk, have been recommended in the place of nitric acid, but these find little employment now.

The products thus obtained appear in commerce in the form of powders varying in colour from almost white to dark brown, through every shade of light yellow and brown. They are reduced to this state after roasting, by crushing in pans or passing through rollers, and then sifting through a rotating silk screen such as is used in flour mills. Schumann (E. P. 1887, 5460) prepares a dextrin free from objectionable smell by agitating starch-milk with 1 p.c. fixed acid, allowing to stand for twenty-four hours, washing the deposited starch free from acid, again converting into a milk of 15° Baumé, and submitting to a steam pressure of three to four atmospheres with  $\frac{1}{2}$  p.c. saturated sulphurous acid solution. The reaction is stopped when the first trace of copper oxide reducing power is observed in the solution, the slight trace of sulphuric acid formed is neutralised with chalk, the syrup filtered through char and evaporated. The commercial dextrin thus obtained is of a brilliant white colour.

The various dextrin syrups are prepared by acting on starch with sulphuric acid or diastase. In the case of diastase, maltose is always produced with the dextrins, and when acids are employed, dextrose also is present. The material employed in the manufacture of these syrups is purified starch of some variety, such as sago, maize, rice, or potato starch, or some starchy material such as maize or rice; the proportions employed are 25 parts material, 75 parts water, and  $2\frac{1}{2}$  parts oil of vitriol. About one quarter of the acid and water are mixed and heated to 55°–60° in a vessel furnished with stirring gear, and the material run into it with continual stirring. Meantime, the remainder of the acid and water is heated to boiling in another vessel also fitted with stirring apparatus and a steam coil; into this the material suspended in and saturated with the acid water is run at such a rate that the temperature is not reduced much below the boiling point. To secure this the steam coil must be sufficiently powerful to admit of a rapid introduction of the mixture. As soon as the starch is dissolved (10–20 minutes or less) the acid is neutralised with the required quantity of chalk, which must be well stirred in, and the neutralised mixture allowed to stand. The clear supernatant liquid is drawn off, and the residue freed from solution by a filter-press. The clear solutions are then concentrated to a suitable consistency in open steam-jacketed pans or in vacuum vessels. These products can be reduced to glassy solids by submitting them in thin layers on shallow plates to a current of hot air or by drying on rotating cylinders.

When diastase is the transforming agent, the starch is mixed with four times its weight of water at 50°, the temperature is then gradually raised to 65–70°, and 2 p.c. of malt added with continual stirring. The temperature is then gradually raised to 73° and kept at that temperature until a portion of the solution cooled no longer gives a blue colour with iodine, but reddish-

violet. The solution is then rapidly raised to boiling, then cooled, filtered, and evaporated as described above.

These products are used as substitutes for the natural gums, and some of the syrups are employed in the manufacture of beer, in confectionery, in leather dressing, and in the preparation of the gelatine rollers used in printing. The products of the action of heat on starch are used for dressing crape, lace, &c., to thicken the mordants and colours used in calico printing. In surgery they are used to fix and thicken bandages, and in pharmacy as carriers for the active agents in pills, powders, tablets, &c. Some varieties of ink are thickened with them, and they are used in a general way for gummings stamps, envelopes, labels, &c. O'S. & H.

**DEXTROSE.** *Dextro-glucose, glucose, starch-, corn-, grape-, honey-, diabetic-sugar.* (Ger. *Krümelmelzucker, Traubenzucker*; Fr. *Sucre de raisin.*)  $C_6H_{12}O_6$ , and  $C_6H_{12}O_6 + H_2O$ .

**Occurrence.**—Reducing sugar or sugars are very widely distributed in nature, but there are few sources from which dextrose has been definitely isolated, and even in these cases it is almost always accompanied by levulose. Among the chief sources may be mentioned honey, most fruits, the sap of some plants and roots, many seeds, and diabetic urine. Blood contains a dextrorotatory sugar, but it has not been established that this is dextrose (Hoppe-Seyler, *Phys. Chem. Berl.* 1881, 430). Seegen and Kratzschmer indicate the presence of dextrose in the aqueous extract of calves' liver. This may be dextrose but it is more probably maltose from glycogen.

**Formation.**—Acids decompose the glucosides into a glucose or glucoses and one or more other bodies; only in a few instances has the glucose been proved to be dextrose, viz. *Amygdalin* (Schmidt, A. C. 119, 92; Hesse, *l.c.* 176, 112). *Populin* (v. Lippmann, B. 12, 1648); *Ruberythric acid* (Liebermann a. Bergami, B. 20, 2247); *Salicin* (Schmidt, A. C. 119, 97; Hesse, *l.c.* 176, 112). In other cases, although the glucose formed is said to be dextrorotatory, reducing, fermentable, and crystallisable, the factors given do not enable one to say with certainty that the sugar is dextrose. These are *Æsulin* (Rochleder and Schwarz, A. C. 87, 186; Zwenger, *l.c.* 90, 76); *Arbutin* (Hlasiwetz a. Grabowski, A. C. Ph. 141, 329); *Coniferin* (Tiemann a. Haarmann, B. 7, 608). The glucoses prepared by the action of acids on other glucosides are not sufficiently characterised to enable one to say whether they are dextrose or not. Certain unorganised ferments act in the same way on the glucosides.

The following carbohydrates yield dextrose alone or with other glucoses by the action of acids:

1.  $\alpha$ - and  $\beta$ -Amylan, dextrose.
2. Cellulose of various kinds, dextrose(?).
3. Glycogen, dextrose.
4. Lichenin.
5. Tunicin.
6. Starch (dextrin), dextrose.
7. Maltose, dextrose
8. Lactose, dextrose and galactose.
9. Sucrose, dextrose and levulose.

Other bodies yield glucose, but as yet we have no direct evidence that dextrose is among

the products, viz. *Melitose (Raffinose)*, *mucilage*, *pectin bodies*, the gums of the arabin group and similar gums, *chondrin* and other gummy bodies of animal origin.

*Preparation.*—Dextrose can be prepared from any of the substances above-mentioned, but it is in many cases difficult to obtain it in any quantity in the pure state. Starch and sucrose are the bodies usually employed, and we find that lactose can also be used with advantage.

(a) A white saccharum (the commercial glucose obtained by the action of acids on starch) with an optical activity approaching that of dextrose is selected. This is scraped as fine as possible, and treated with boiling ethyl alcohol of sp.gr. .820. On cooling, the clear saturated solution is separated from the undissolved syrup and a little previously prepared dextrose added to it. Crystallisation soon begins and continues for some time, a crop of fairly pure dextrose is thus obtained. Further purification can be effected by melting the crystals in 8-10 p.c. boiling water and adding dry boiling methyl alcohol until a slight cloud is produced. Anhydrous dextrose in a state of great purity separates abundantly from this solution. Or the saccharum is melted in 5 or 6 p.c. water, allowed to crystallise, the crystals pressed and further purified by treatment with methyl alcohol as described.

(b) A 25 p.c. aqueous solution of crystallised sucrose is taken and heated to 50°-55° and 2-3 p.c. pressed brewers' yeast stirred in (Tompson, E. P. 8686, 1884) the temperature is maintained for 2-3 hours, when the sucrose is completely inverted, that is converted into dextrose and levulose. The solution is then evaporated in a vacuum to a syrup, sp.gr. 1.5 or thereabouts. On standing for a short time this solidifies to a crystalline mass; it is washed with cold ethyl alcohol, sp.gr. .830, and the residue dissolved to saturation in alcohol of the same strength. Dextrose soon begins to crystallise out; the crystals can be further purified by dissolving in methyl alcohol and recrystallisation.

Sucrose may also be inverted by digestion with sulphuric acid, the acid separated by baryta water, and the filtrate from the barium sulphate evaporated to a syrup and treated in the way mentioned. Inversion by yeast yields the best result. Soxhlet (J. pr. [2] 21, 242) recommends that inversion be effected by alcoholic hydrochloric acid. 480 c.c. of strong hydrochloric acid are mixed with 12 litres of alcohol, sp.gr. .810, in a glass vessel, the mixture heated 45-50°. 4 kilos. powdered sucrose stirred in, and the whole maintained at that temperature for two hours. When cool, a little previously prepared anhydrous dextrose is added, and in a few days there is an abundant crystallisation of dextrose. This can be purified by crystallisation from methyl alcohol. Should any colour be developed, the aqueous solution of sugar is treated with animal charcoal and again concentrated in a vacuum. Under such circumstances it is better to begin again, for if proper care be taken no colour need be produced.

An aqueous solution containing 25 p.c. lactose and 3 p.c. sulphuric acid is digested in a water bath for three hours, care being taken by continued agitation that no colour is developed, the sulphuric acid is separated by baryta

water and the filtrate concentrated to a syrup containing 76-80 p.c. solid matter. On standing this solidifies, and after a few days is treated with boiling methyl alcohol; this dissolves out the dextrose, leaving the galactose undissolved; the former soon crystallises from the saturated methyl alcohol. A recrystallisation yields the pure body in moderately large, well-defined crystals.

Hydrous dextrose  $C_6H_{12}O_6 \cdot H_2O$  can be obtained from any of the above preparations by dissolving in 12 to 20 p.c. water, and allowing to crystallise. If honey is used as a source of dextrose, any sucrose it may contain should be inverted by yeast or acids, and the residue obtained by evaporation crystallised from methyl alcohol as in the case of inverted sucrose. A pure product may be obtained by a few crystallisations.

*Properties.*—Dextrose crystallises out of strong (93-95 p.c.) ethyl or methyl alcohol in the anhydrous state  $C_6H_{12}O_6$ , and from concentrated aqueous solutions at 30°-35°, with special treatment, crystals of this composition may also be obtained. The crystals formed in aqueous solutions at ordinary temperatures contain a molecule of water of crystallisation  $C_6H_{12}O_6 \cdot H_2O$ . The anhydrous sugar forms white crystalline crusts or powder and, when it separates from the solvent slowly, fairly well-defined glassy prisms; the hydrous body crystallises in cauliflowerlike masses, but with care and slow crystallisation well-defined crystals can be obtained. Both bodies dissolve easily in water, the anhydrous one with evolution of heat. The hydrous body dissolves freely in strong ethyl and methyl alcohol, especially on the application of heat, but the anhydrous body is practically insoluble in these liquids. An aqueous solution of dextrose containing 10 grams anhydrous dextrose in 100 c.c. of solution at 17.5° is said to have a sp.gr. 1.0381. This is probably low—the number 1.0385 being more correct. Its solutions are optically active, i.e. possess the power of rotating the plane of polarisation of a ray of polarised light. The rotation is right-handed. Hitherto, various values have been given for the constant expressing this activity, the variation being due to imperfect standards and to the impurity of the specimens of sugar examined. Recently Hesse (A. 176, 106) and Tollens (B. 17, 2234) have carefully determined this constant, and the latter's results are expressed by the formula

$$[\alpha]_D = 52.5^\circ + .018796 P + .00051683 P^2$$

for the dry sugar, and

$$[\alpha]_D = 47.73^\circ + .015534 P + .0003883 P^2$$

for the hydrous body  $C_6H_{12}O_6 \cdot H_2O$ , in which  $P$  = the percentage of anhydrous and hydrous sugar in solution. In dealing with solutions containing 10 p.c. dry sugar the factor  $[\alpha]_D = 52.7$  and  $[\alpha]_D = 58.3$  may be used. The optical activity of dextrose solution is not materially affected by temperature. The activity is nearly twice as great in freshly prepared solution, diminution taking place slowly in cold but rapidly in boiling solutions until the constant value is arrived at. It is only crystallised dextrose that exhibits this property of bi-rotation, as it is called, dextrose fused and allowed to solidify does not show it (Hesse, A. 176, 113). The solution of dextrose in strong alcohol retains the power of

bi-rotation. Potash, soda, lime, and such bodies which act on dextrose naturally reduce its optical activity. Hydrated dextrose begins to fuse at  $80^{\circ}$ , but inasmuch as a portion of the water is expelled at a lower temperature and continues to be expelled, complete fusion is not effected at  $100^{\circ}$ . The melting point of the anhydrous sugar is about  $146^{\circ}$ . In a vacuum over sulphuric acid the hydrate parts with the greater portion of its water, the remainder of which can be easily eliminated at  $100^{\circ}$ , but if the substance is at once heated to  $100^{\circ}$ , it fuses partially, becomes coloured, and the water is got rid of with difficulty, if at all completely. When the dry body is heated to  $170^{\circ}$ , the elements of a molecule of water are eliminated, dextrosan  $C_6H_8O_5$ , being produced. If the temperature is increased that body is caramelised and charred. Dextrosan is again converted into dextrose by digestion with water or dilute acids. If the temperature is raised to  $200^{\circ}$  and maintained at that point for a little time, gas, water, and volatile acids are given off, and if the heating is continued without being increased until these products cease to be evolved, the brownish black residue (caramelised mass) becomes gradually solid. This substance is soluble in water, completely if the temperature was not too high, and constitutes the colouring matter used in wine, beer, cookery, &c. Should the heat be further continued so that the body is destructively distilled, carbon mon- and di-oxide, and marsh gas are evolved, aldehyde, furfur-aldehyde, acetone, met-acetone, propionic, acetic, and formic acids distil over, and a black carbonaceous mass is left.

Dextrose is dissolved by concentrated sulphuric acid without blackening, a conjugate acid, dextrose-sulphuric, being formed (Musculus a. Mayer, B. 14, 850) and from this a dextrin-like body or didextrose is precipitated in combination with alcohol on standing in contact with strong alcohol for some time. If dextrose is boiled with dilute sulphuric acid the sp.gr. of the solution gradually increases for some time, apparently from the fixation of the elements of water. On continued boiling the solution becomes coloured and finally brown humus substances, lavulinic and formic acids are produced (Malaguti, A. Ch. [2] 59, 407; Tollens, A. 206, 207). Digestion with dilute hydrochloric acids produces similar results, but more rapidly. For action of acids on dextrose v. also Conrad a. Guthzeit, B. 18, 439, a. 19, 2569.

Alkalis decompose dextrose quickly on heating, slower in the cold, with the production of, amongst other things, acetol and acetone, which are volatile, and of lactic, acetic, and formic acids which remain combined with the alkalis; other substances are formed at the same time, such as glucinic, saccharumic, and japonic acids, but further knowledge is required regarding them. When potash is used in these experiments oxygen is absorbed. With calcium hydroxide saccharin or calcium saccharinate is produced; this is not one of the products of the action of potash. Lactic acid and other bodies are formed at the same time.

Thenard (C. R. 52, 444) obtained bitter-tasting bodies containing 10-19.3 p.c. nitrogen by acting with ammonia on dextrose; they absorb

oxygen from the air, and have much in common with some nitrogenous humic acids. Similar products are produced by the action of barium nitrate on dextrose (Thenard, C. R. 52, 795). Tamet (Bl. [2] 44, 102) obtained volatile  $\alpha$ -glucosine  $C_6H_{10}N_2$ , b.p.  $136^{\circ}$ , and  $\beta$ -glucosine  $C_7H_{10}N_2$ , b.p.  $160^{\circ}$ , by heating dextrose with strong ammonia. When dextrose is heated with aniline, dextrose anilid is produced (Schiff, A. 140, 123; Ssorokin, B. 19, 298).

Nascent hydrogen converts dextrose in alkaline solution into mannitol, but not in neutral or acid solutions (Linnemann, A. 123, 136). Even under the most favourable conditions the yield does not exceed 10 p.c. of the dextrose employed. A varying quantity of other alcohols of the fatty series is simultaneously produced when the reaction is allowed to take place at a high temperature.

Oxygen has no action on dextrose in neutral or acid solutions, but alkaline solutions absorb the gas. Ozone oxidises it to formic acid, saccharic acid &c. being produced. Strong nitric acid converts dextrose into saccharic acid, and finally into oxalic, carbonic, and formic acids (Liebig, A. 113, 1; Heintz, P. 51, 183; Hornemann, J. pr. 89, 304; Kiliani, A. 205, 172; Guerin-Varry, A. 8, 31; Sohst and Tollens, C. Z. 11, 99). Treated with chlorine or bromine in the presence of water, the resulting product yields gluconic acid when submitted to the action of silver oxide (Hlasiwetz and Habermann, A. 155, 122; 156, 253; Kiliani, A. 205, 182; Kiliani and Kleemann, B. 17, 1298; Herzfeld, A. 220, 335 and 358).

In presence of alkalis, iodine yields with dextrose, as with many other bodies, iodoform (Lieben, A. Suppl. 7, 228; Herrmann and Tollens, B. 18, 1335; Millon, C. R. 21, 828).

Dextrose in alkaline solutions reduces the oxides of gold, platinum, silver, mercury, bismuth, lead, copper, iron, manganese, &c.; in the case of gold, platinum, silver, and mercury, the reduction is complete, the metal being formed; in the other cases lower oxides are produced. Ferrocyanide of potassium, indigo, picric acid, litmus, and such substances are also reduced by dextrose in alkaline solution. The products from the dextrose are not the same in all cases, but they consist chiefly of carbonic, formic, oxalic, and glycolic acids, other products being also formed; v. Kiliani, A. 205, 182; Kiliani and Kleemann, B. 17, 1298; Herzfeld, A. 220, 335 and 358; Tollens, B. 16, 921; Habermann and Hönig, B. 15, 2624; Pflüger's Arch. d. Physiol. 22, 325; B. 13, 2096 a. 2442; Reichardt, A. 127, 297; Felsko, A. 149, 356; Beyer, A. 131, 353; Claus, A. 147, 115.

Under the influence of *Saccharomyces cerevisia* and other organisms, dextrose ferments yielding alcohol and carbon dioxide as the chief products, but glycerol, succinic acid, and other bodies are formed at the same time, the proportions of these bodies varying materially with the organisms and the conditions under which the growth takes place. In the presence of growing bacteria of various species dextrose yields many products, one species converts it into lactic acid, another into butyric, another into cellulose, and so on (v. FERMENTATION).



With sulphuric acid dextrose forms several conjugate acids, the barium salts of which are soluble (Peligot, J. pr. 15, 105; Claesson, J. pr. [2] 20, 1 and 18). They are produced by dissolving dextrose in the cold in strong sulphuric acid, or acting upon the dry body with chlorosulphonic acid. The constitution and composition of these bodies require further investigation.

A mixture of sulphuric and nitric acids converts dextrose into a nitro body (Carey-Lea, Bl. [2] 10, 415), which is explosive. It is obtained by dissolving the gradually crystallising mass produced in ether alcohol, and precipitating with water.

A dextrose phosphoric acid  $C_6H_{11}O_5 \cdot H_2PO_4$  is said to exist (Anato, B. 4, 413).

Various derivatives of dextrose in which the anhydride of an organic acid displaces hydroxyl are known and have been studied by Berthelot (A. Ch. [3] 60, 93; *Chimie organ. fondée sur la synthèse*, 2, 289); Schützenberger and Naudin (Bl. [2] 12, 107 a. 204); Liebermann a. Hörmann (B. 11, 1619); Herzfeld (B. 13, 265); Franchimont (B. 12, 1939). They are amorphous substances formed by the action of the anhydride or sodium salt of the acid on dry dextrose, and can only be purified with difficulty.

Compounds of dextrose with bases have been studied; they are very unstable and rather indefinite in character and composition. It appears that in the compounds of sodium and potassium the metal displaces hydrogen of the dextrose, potassium dextrosate being  $C_6H_{11}KO_6$  (Hönig a. Rosenfeld, B. 10, 871), and the sodium compound  $C_6H_{11}NaO_6$ . These are prepared by adding ether and an alcoholic solution of soda or potash, or the alcoholate of these bases, to an alcoholic solution of dextrose cooled in a freezing mixture; the precipitate is washed with strong alcohol and ether, and dried over sulphuric acid. The compounds with the alkaline earths seem to be differently constituted, the earthy oxide being simply added on to the dextrose molecule. With lime several compounds have been described containing varying proportions of dextrose, lime, and water; we have  $C_6H_{12}O_6 \cdot CaO$ ,  $(C_6H_{12}O_6)_2 \cdot CaO \cdot H_2O$ , and other bodies (Peligot, J. pr. 15, 105; Brendecke, Arch. d. Pharm. [2] 29, 84). Compounds of the same nature and composition exist containing barium oxide (v. Lippmann, Zuckerarten, 45; Peligot, *loc. cit.*; Brendecke, *loc. cit.*). Strontium and magnesia also yield compounds of a like nature (Franchimont, B. 12, 1939). Like the compounds with alkalis, these bodies are prepared by adding solutions of the earths to strong alcoholic solutions of dextrose, washing with strong alcohol, and drying over sulphuric acid.

With solutions of the oxides of lead and copper, dextrose yields compounds of much the same nature as with the alkaline earths. Neither acetate nor subacetate of lead gives a precipitate with dextrose, but solutions of these bodies in ammonia yield precipitates in which no doubt the lead oxide is added on to the dextrose in the same way as the alkaline earths; we have  $(C_6H_{12}O_6)_2 \cdot 3PbO$ , &c.

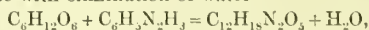
Alkaline, but not neutral, solutions of dextrose dissolve copper oxide (Worm-Müller and Hagen, Pflüger's Archiv, 22, 325), and from these solu-

tions soda or potash in proper proportions precipitates compounds of dextrose and copper oxide in which the proportion of the former to the latter may vary from one to one to one to five (Fileti, B. 8, 441; Salkowski, B. 12, 701). By a proper addition of soda the whole of the dextrose can be precipitated from a solution containing that body and copper sulphate.

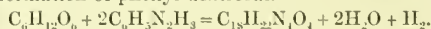
Dextrose combines with sodium chloride, bromide, and iodide, forming well-defined crystallised compounds; the body  $(C_6H_{12}O_6)_2 \cdot NaCl \cdot H_2O$  crystallises from diabetic urine (Peligot, J. pr. 15, 88; Pasteur, A. Ch. [3] 31, 92). The same body can be obtained by making a strong solution containing dextrose and sodium chloride in molecular proportions and allowing it to evaporate slowly at a low temperature. It crystallises in well-defined glassy crystals. Frequently, however, bodies of the composition  $C_6H_{12}O_6 \cdot NaCl$  and  $C_6H_{12}O_6 \cdot 2NaCl$  crystallise out (v. Lippmann, Zuckerarten, 45; Städeler, C. C. 1854, 930). The sodium bromide compound  $(C_6H_{12}O_6)_2 \cdot NaBr$  crystallises in white plates (Hönig and Rosenfeld, B. 10, 872; Stenhouse, A. 129, 286), and the sodium iodide compound  $(C_6H_{12}O_6)_2 \cdot NaI$  is very readily obtained (Gill).

Kiliani (B. 19, 767 a. 1128), by acting on dextrose with hydrocyanic acid, obtained a cyanhydrin which on treatment with baryta yields ammonia and the barium salt of a dextrose carbonic acid, hex-hydroxy-heptylic acid  $C_7H_{13}(OH)_6N_2$  (Schützenberger, Bl. [2] 36, 144; Maquenne, Bl. [2] 43, 530). This yields a lactone  $C_7H_{12}O_6$ , which on treatment with iodine and phosphorus is converted into normal heptylic acid  $C_7H_{15}O_2$  and the lactone  $C_7H_{12}O_6$ .

Recently Fischer (B. 17, 579) and others have described a very interesting series of bodies in which dextrose enters into combination with the hydrazines, and Griess and Harrow (B. 20, 281, and 2205) have shown that the aromatic amines, dianines, &c., form similar compounds. When concentrated solutions of dextrose and phenylhydrazine are mixed in the cold, the two bodies unite with elimination of water



dextrose phenylhydrazine being produced. In dilute solutions, and at temperatures near the boiling-point of water, one molecule of dextrose combines with two of phenylhydrazine, with the elimination of water and hydrogen and the formation of phenyl-dextrosan



The hydrogen is not evolved as such, but acts on part of the hydrazine, converting it into aniline and ammonia. Dextrose-phenylhydrazine forms colourless needles which melt at  $144-145^\circ$  (E. Fischer, B. 20, 824). It is converted into phenyl-dextrosazon by excess of acetic acid. This body is also formed by heating 1 part dextrose, 2 parts phenylhydrazine hydrochloride, 3 parts sodium acetate, and 20 parts water in a water-bath; it gradually separates from the mixture in yellow needles, and can be purified by one or two crystallisations from alcohol. Its melting-point is  $204-205^\circ$ . It is but little soluble in water, but easily in alcohol. It reduces alkaline copper oxide solution, and is laboratory (Fischer a. Tafel, B. 19, 1920; 20, 217 a. 2566). According to Fischer (B. 19,

1920), it is reduced by zinc-dust to iso-glucosamine, which yields levulose on treatment with nitrous acid.

Other dextrazons, compounds with the tolyl hydrazines, &c., have been described (Raschen, A. 239, 229; Roder, A. 236, 172).

Strong hydrochloric acid decomposes dextrosazon into phenyl hydrazine, which separates in the form of hydrochloride and oxyglucose (glucoson)  $\text{CH}_2\text{OH}(\text{CH.OH})_3\text{CO.CO.H}$  (Fischer, B. 21, 263). It is reduced by zinc-dust and acetic acid to levulose (*l.c.*).

Grüss a. Harrow (B. 20, 281 a. 2205) have described a series of bodies obtained by acting on dextrose with aromatic diamines and di-amido-acids. Di-dextro-*o*-diamidobenzol  $\text{C}_6\text{H}_4\text{N}(\text{N.C}_6\text{H}_5\text{O}_2)_2$  is formed, with the elimination of two molecules of water when ortho-diamidobenzol is allowed to act on dextrose in aqueous solution in the proportion of one molecule of the former to two of the latter. Anhydro-dextro-*o*-diamidobenzol  $\text{C}_6\text{H}_2\text{N}_2\text{C}_6\text{H}_4\text{O}_2$ , water, and hydrogen are formed when the action takes place in acid solution, and dextro-*o*-diamidobenzol  $\text{C}_6\text{H}_4(\text{NH})_2\text{C}_6\text{H}_4\text{O}_2$  is obtained by concentrating the mother liquor from the di-dextro-compound. With *m-p*-diamido-toluol, dextrose yields similar compounds. Dextrose combines with  $\gamma$ -diamido-benzoic acid, with the formation of dextro- $\gamma$ -diamido-benzoic acid  $\text{C}_6\text{H}_3(\text{COOH})(\text{NH})_2\text{C}_6\text{H}_4\text{O}_2$ .

*Manufacture of commercial dextrose*—*i.e.* dextro-glucose, glucose, saccharum, saccharine, &c.—These products, varying much in character and composition, are all prepared by the action of acids on starch or starchy substances, such as rice, maize, &c., and when these latter are the raw material it has been proposed to employ the combined action of diastase and acids. When starch is acted upon by dilute acids it is dissolved, dextrans and maltose being produced. These bodies, by the further action of the acid, yield dextrose; this itself does not resist the action of acids, so that during the process of conversion a portion of it is attacked, with the production of substances imperfectly studied (*v. GALLSIN*). We know, however, that these bodies existing in the commercial products are unfermentable, and that a solution of dextrose, when subjected to the continued action of dilute acids, increases in gravity and diminishes in optical activity, pointing to the destruction of the sugar and the formation probably of higher-hydrated carbohydrates  $\text{C}_6\text{H}_{11}\text{O}_5$ , the elements of water being assimilated. Heron (S. C. I. 7, 271) states that by heating commercial glucose with 3 p.c. sulphuric acid for 1 hour at 160°, 34 p.c. of these bodies are formed. This may be the case with invert sugar, but it seems hardly probable that a starch product would be changed so quickly.

The phases of the action of dilute acids on starch are easily followed. After heating has been continued for a short time a portion of the solution cooled ceases to give a blue colouration with iodine; this indicates absence of starch; in the place of this a reddish-brown colouration is produced, this indicates the presence of  $\alpha$ -dextrin. After a time this disappears, and at length the solution ceases to give a precipitate when to

a portion of it twice its bulk of alcohol (sp.gr. 820) is added, or when to a portion from which the sulphuric acid has been separated by baryta, ammoniacal lead acetate is added. This establishes the absence not of maltose but only of dextrin. There is no ready method by which the complete conversion of starch into dextrose can be ascertained, yet if pure starch be employed and the quantity of sulphuric acid carefully gauged, a determination of the sp.gr. and optical activity of a cooled and filtered sample could be done with sufficient rapidity and accuracy to give a fair idea of the extent of the conversion. Even when impure starch or starch-containing material is employed, the analyses of a few conversions in which the temperature and proportion of material, water, and acid were kept constant would establish a time factor for the most perfect and desirable conversion. The processes involved in the manufacture may be conveniently arranged as follows:

- The conversion.
- The neutralisation.
- The filtration.
- The decolourisation.
- The concentration.
- The purification.

*a. The conversion.*—In this country the materials chiefly employed in the manufacture of commercial dextrose are sago, maize, and rice starch, finely ground rice itself as well as granulated maize and rice being at times used. Potato starch is also used in Germany. In America green maize starch is the chief material, hence the term 'corn sugar.' The acid usually employed is sulphuric, but hydrochloric and nitric acids have been recommended, as well as a mixture of nitric and sulphuric acids. The use of sulphurous and ortho-phosphoric acids has also been advocated. The proportions of material, water, and acid generally employed in the case of sulphuric acid are 100:250:5, and when green starch, *i.e.* undried purified starch, is used,  $1\frac{1}{2}$  parts are taken instead of 1 part dry starch. When pressure converters are used the acid can be reduced to 0.5 p.c. John (Berz. Jahresh. 1815, 16, 262) proposed to complete the action of the sulphuric acid by the subsequent addition of a small quantity of nitric acid and re-boiling the solution, a more thorough conversion of the starch into dextrose being thus obtained. The difficulty of removing the soluble nitrates formed on neutralisation arose, and no solution of the problem was at that time effected. Kröthe (Vierteljahrsschr. für tech. Chem. 1869, 449) also employed nitric acid for the more rapid and thorough saccharification of starch. For the production of syrup he takes 10 lbs. sulphuric and 1.2 lbs. nitric to 1,000 lbs. green starch and 130 gal. water; the time of boiling is from three-quarters to one hour. If solid sugar be required, the proportions are 15 lbs. sulphuric and 2 lbs. nitric acid to 1,000 lbs. green starch; time required from one and a half to two hours. He used sulphurous acid to destroy the nitric acid, and neutralised with chalk and sodium carbonate.

Seyberlich and Trampedach (E. P. 8000, July, 1885) recommend dilute nitric acid alone ( $\frac{1}{2}$  p.c. on air-dried starch). Digestion is continued to the required extent, the concentrated

liquid neutralised with chalk and made alkaline with sodium carbonate. The filtered solution is evaporated *in vacuo* to 33°-36 B., when, on cooling and standing for a time, dextrose separates out in crystals so large that they may be separated from the syrup by the centrifugal machine. Another crop of crystals may be obtained by evaporating the syrup from the centrifugals, after which the residue is treated with sufficient sulphuric acid to liberate the nitric acid; the latter may be again used for the saccharification of fresh starch after filtration of the precipitated gypsum. According to a later patent (G. P. 39,573, Nov. 9, 1886) the nitric acid is removed by the addition of sulphurous acid to the hot solution, nitric oxide being quantitatively evolved and a corresponding amount of sulphuric acid formed. The excess of sulphurous acid is got rid of by boiling and the introduction of steam into the liquid; the solution is neutralised with chalk, rendered alkaline with sodium carbonate, and the sugar concentrated as before (v. also D. P. J. 271, 512). This process seems not to have come into use.

Johnson (E. P. 1875, 810) substitutes hydrochloric acid for sulphuric acid, and employs rice or maize almost in the dry state as the raw material. The grain is allowed to saturate itself in a suitable vessel with water containing HCl equal to 2 p.c. of grain taken, and then washed free from the solution. Sufficient acid of the same strength is now added to cover the grain and allowed to permeate it, after which the excess is drained off. Thus treated, the grain retains 40-60 p.c. of its weight of dilute acid; it is then introduced into a specially constructed gun-metal converter (described below), and steam admitted to bring the pressure up to 75 lbs. per square inch. In about a minute the starch is dissolved, and water at 150°, equal in weight to the material taken, is injected under pressure; the above pressure being maintained, conversion is then completed in a further minute. Twelve charges, each of 400 lbs. grain, can be converted in one hour. The neutralisation is with chalk in the usual way. Purified starch is converted in the same apparatus by saturating it with dilute HCl, drying, introducing it in this state into the converter, and treating otherwise as the raw grain.

Humphreys (U. S. P. 25, 1887) treats soaked and crushed maize at 100° with sufficient acid to dissolve the starch, the proportion should be such as to make the solution 10-12° B. The germs which float on this solution are skimmed off and pressed for oil, the remaining solids are filtered out and pressed for fodder, and the solution treated in the usual way for glucose.

Endemann (B. P. 6,176, 1882) employs phosphoric acid, and uses 1 part ortho-phosphoric acid, 20 parts starch, and 40 parts water; a closed converter is employed and a temperature of 140°. The acid is separated by an equivalent quantity of lime.

Soxhlet (E. P. 7,098, June 10, 1885) uses both diastase and acid. Rice, or the starch residue from the manufacture of rice-starch, is finely ground and stirred up with water to a thick paste. This is allowed to run into boiling water, and kept boiling for an hour. The gelatinised starch is cooled to 50-58°, and a malt infusion

(2 parts malt to 100 parts rice) run in. If the fluid should be acid, it is neutralised with soda. After the liquid has been boiled for a few minutes the precipitated albinoids are filtered off, and the solution acted on with sulphuric acid either under ordinary or increased pressure. The subsequent operations are as usual.

*Converters.*—The apparatus in which the conversion of starch is brought about are of various types. Fig. 1 represents an open converter in which the action takes place at the boiling temperature of the liquid. This consists of a stout wooden vat furnished with a steam coil (cc)

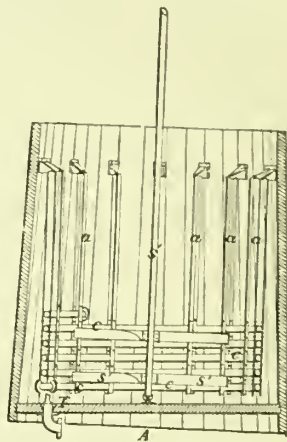


FIG. 1.

of lead or gun-metal suspended on stirrups *aa* to prevent disruption by unequal contraction and expansion, and a stirring-gear *s* by which the contents are kept in motion. At *t* are shown a plug and pipe for discharging the converter's contents. Fig. 2 shows the ground plan of this ap-

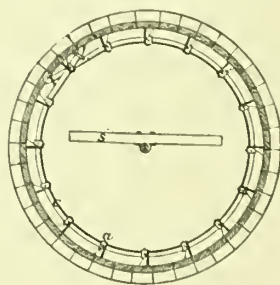


FIG. 2.

paratus. Fig. 3 represents Hoffmann's converter. It consists of a stout, well-hooped, wooden vat of the same construction as the previous apparatus, only that it is supplied with a cover *r* furnished with a manhole *h*, a safety-valve *v*, and a pressure-gauge *m*. There is also stirring-gear in this vessel arranged as shown in fig. 4 or 5. In the former the gear is driven by a spur-wheel *g* from below, in the latter from above. The heat is supplied by a 'raw' steam pipe *l* instead of a coil.



This apparatus is usually worked at a pressure of 15-20 lbs. per square inch.

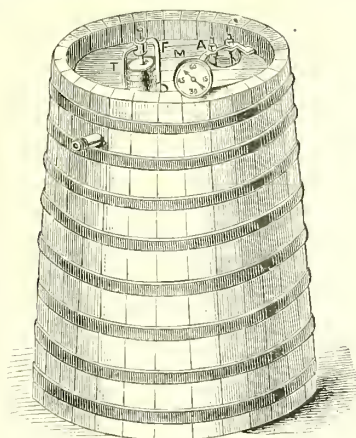


FIG. 3.

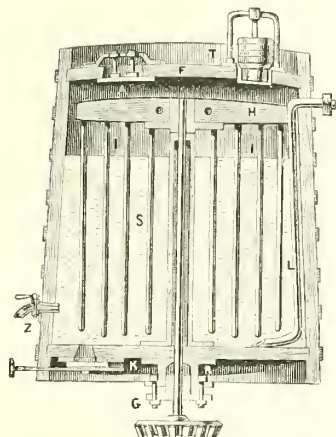


FIG. 1.

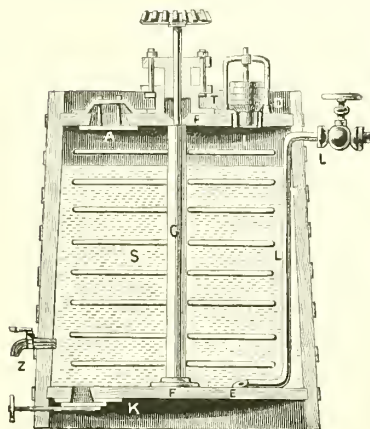


FIG. 5.

Mambre (E. P. 552, 1864) makes use of a strong lead-lined iron vessel as a converter (fig.6).

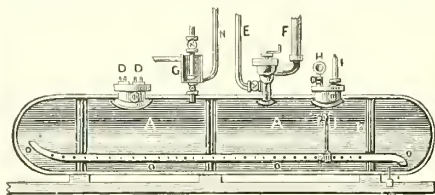


FIG. 6.

Steam is supplied by the tube o o o, which is furnished with many perforations. g is the charging tube, and n one for admitting water. ce are the manholes, in the cover of one of which a pressure-gauge, u, and a thermometer, t, are fitted, and in that of the other safety valve, v. e is a tube for the extraction of volatile, disagreeable-smelling products, which are always evolved when acids act on only moderately pure starch. r is a tube for the escape of steam. On the outside is a water-gauge j to indicate the level of the liquid in the vessel. The discharge-pipe is shown at f. The lead lining of this vessel is kept in place with difficulty; but this is partially obviated by perforating the iron coating so as to admit of the escape of vapour of water or air confined between

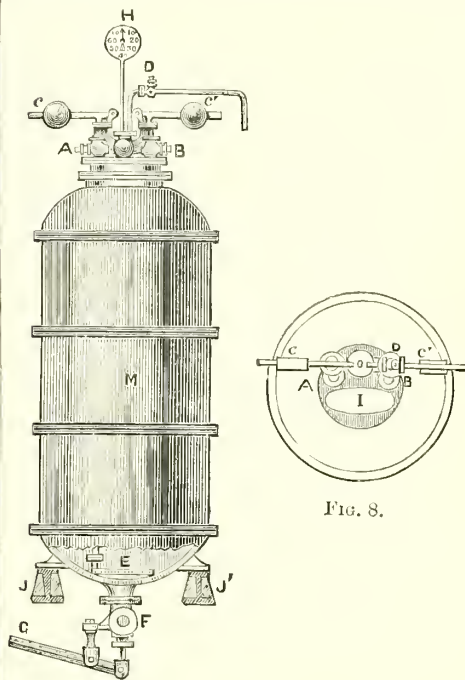


FIG. 7.

the iron and lead layers. At present gun-metal vessels replace the lead-lined iron ones. The position of the cylinder is upright instead of horizontal, and the arrangements of the parts slightly different. Fig. 7 represents the most recent form. It consists of a gun metal cylinder

is placed in an upright position on the girders J J'. The steam enters through the cock A and is conducted to the bottom of the converter by a pipe which terminates in a perforated coil K. The charge is introduced through the cock B. D is a sampling tap, the pipe connected therewith passing almost to the bottom of the cylinder. C C' are safety valves, but inasmuch as the converter is made to withstand much greater pressure than the boilers supplying the steam, their services could be dispensed with. F is the discharge valve actuated by the lever G. H is a steam pressure gauge. A plan of the top is shown in fig. 8, I being a manhole, the other parts are lettered as in fig. 7. While the charge is being run in through B, steam is admitted at A; B is closed as soon as the whole charge is in and the pressure rapidly raised to 70-80 lbs. per square inch. As soon as the conversion is complete, the charge is forced through the valve F and conveyed through a pipe to the neutralising vats.

Johnson (E. P. 1875, 810) has introduced a modification of this apparatus. The parts are essentially the same, the modification being such as to enable conversion to be made with moderately dry material.

Fig. 9 shows the working parts of this converter. The charge of prepared material is

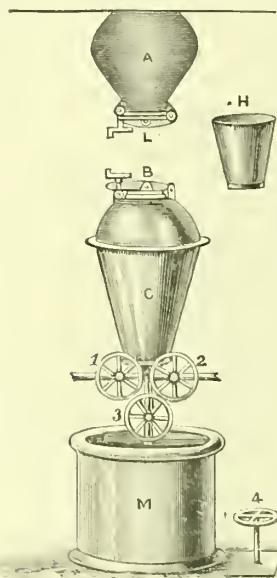


Fig. 9.

measured into the leaden hopper A attached to the floor above. The lid B of the converter C is then opened and the funnel-shaped copper vessel is fitted into the opening; the slide valve L is then opened and the charge allowed to pass into the converter. When this is accomplished, the funnel is removed and the lid B screwed tight, taps 3 and 2 are closed and steam from the boilers admitted through tap 1; the pressure being rapidly brought to 75 lbs. per square inch. At the end of a minute the charge becomes

liquid; meantime a quantity of water equal in bulk to the charge at a pressure of 80 lbs. is measured by pressure gauge into the vessel M by tap 4; tap 1 is then closed, tap 3 opened and the superheated water from M forced into the converter, this tap is again closed and the pressure kept up by again admitting steam through tap 1. When the conversion is completed, which is generally in about 3-4 minutes, the charge is forced, by opening tap 2, into the neutralising vat. At the top of the steam inlet to converter there is a valve opening upwards: this prevents the return of any of the contents of the converter into the measuring vessel. The converter is made of an alloy of 11 parts tin and 89 parts copper, both metals being as pure as possible, care being especially taken that they are free from zinc. This alloy resists the action of dilute acids for years.

Many other forms of closed converter are in use, the material being copper or gun-metal, in which the heat is supplied by a steam coil or naked steam, or both. In these the parts are essentially the same as in the apparatus described.

The operations involved in the manufacture, whatever converter is used, are as follows. Half the sulphuric acid is mixed with half the water in a separate vat constructed as the converter (fig. 1), with or without coil, and at such a temperature that the heat of the dilute acid will be just less than the gelatinising point of the starch of the material employed. This vat is furnished with stirring gear, and placed under a hopper, in which is stored the starch or starchy substance. When the dilute acid is at the right temperature the material is allowed to flow into it, the stirring gear being kept in motion; a milk of starch in dilute acid is thus obtained. Meanwhile the remaining half of the acid and water are introduced into the converter and heated to boiling, then the starch-milk is run in at such a rate that the temperature does not fall far below boiling, and the introduction should be effected as rapidly as possible; this is accomplished by having a coil sufficiently powerful, in the case of the open converter, and a sufficient supply of high-pressure steam, in the case of the closed ones. With an open converter we have seen the product known as dextrin-maltose (E. P. 1874, 3909), the proportion of material, water, and acid being those given above, produced from maize starch in one hour, and from sago in a slightly less time, and a product obtained after three and a half hours' digestion, which yielded by the usual after-treatment, but without the use of charcoal, a solid sugar, of fair average colour and normal composition. The time required in the pressure converters is less; in the wooden vessels with a steam-pressure of 15-20 lbs. per sq. in., if the steam injector is sufficiently powerful to keep the temperature up to boiling and admit of the rapid introduction of the acid starch milk, dextrin-maltose composition can be arrived at in 35 minutes with maize starch and in a slightly less time with sago, and a solidifiable sugar in less than 2 hours. The higher the pressure employed, the less time required for conversion; but, as has been pointed out above, the time factor can easily be arrived at for any material by an exa-

mination of the products of a few conversions at different stages. Johnson, using starch saturated with hydrochloric acid (about 0.25 p.c. real acid on the starch), says he obtains glucose in 1-2 minutes.

*b. The neutralisation.*—Finely-ground chalk is used to neutralise the acid employed in the conversion. The chalk is converted into a milk with water, and gradually introduced into the converted liquid. This is usually done in a separate vessel. The milk of chalk is made in a small vat fitted with stirring gear, and then run through properly gauged taps, with the converted liquid, into a vat, also furnished with stirring gear. About 12 lbs. of powdered chalk are taken for every 10 lbs. sulphuric acid employed; this is more than the theoretical quantity, but it is found to answer in practice, owing no doubt to the insolubility of a portion of the chalk. The neutralised liquid is kept stirred for some time, and is then allowed to rest. It is found best to allow it to cool and settle gradually, and then draw off the clear portion; but where vat room is a consideration the neutralised liquid is run immediately to the filter presses. Calcium hydroxide and other alkalis have been mentioned as neutralising agents, but calcium carbonate gives the best results, as the least trace of alkali in excess colours the liquid by acting on the dextrose.

*c. The filtration.*—The neutralised liquid can be freed from calcium sulphate and other insoluble matters by filtration through Taylor's filter bags, or, as is very generally the case now, through presses of one kind or another, being various improvements on Needham and Kite's filter-press. One of the best forms of this made in this country is Johnson's (*v. FILTRATION*).

*d. Decolourisation.*—The clear filtered solution, if too highly coloured, is passed through animal charcoal towers, of the same construction as those described under SUGAR. Sulphurous acid is sometimes used in bleaching the product. Von Korvin-Sakovitz a. Rosenblum (*G. P.* 2418, Feb. 1, 1883), decolourise converted syrup by treating it at 45° with 2 p.c. of potassium permanganate on the starch employed, and filtering the decolourised syrup as usual.

*e. Concentration.*—This operation is now, as a rule, effected in vacuum pans (*v. SUGAR*), and is considered complete when the syrup contains about 82 p.c. solid matter, *i.e.*, reaches a sp.gr. 1.50. It is then run into moulds, usually cone-shaped vessels, in which on standing and cooling it solidifies after a short time. This is hastened by the introduction of some previously solidified sugar. The solidified mass extracted from the mould by a short immersion in hot water is broken into irregular lumps, in which form it appears in the market. The colour of the commercial parcels varies from pure white to dark brown; this depends on the character of the material employed (the purity and variety of the starch), on the mode of conversion, and the extent to which the decolourisation was carried. The composition is also very variable, but the constituents in all are the same, *viz.*, dextrose, maltose, dextrin, unfermentable organic bodies, and ash. Very few samples contain dextrin, some few maltose, and the proportion of unfermentable bodies varies very much,

being sometimes as high as 15 p.c. The syrups contain a large percentage of dextrin and maltose.

*f. Purification (refining).*—For some purposes it is desirable to eliminate the impurities and to furnish pure dextrose as a commercial article.

Soxhlet (*G. P.* 17,465 and 17,520, October 11, 1881; *J. pr.* 21, 227) proposed to effect this object by evaporating the clear colourless converted solution in a vacuum to about 85 p.c. solid matter (sp.gr. 1.520), dissolving the syrup in boiling strong methyl alcohol, and running the solution into cone-shaped vessels capable of being closed at the apex. The sugar crystallises in from two to three days, and the mother liquor can be drawn off. A dense hard sugar is obtained by feeding the crystals with a solution containing 100 parts concentrated syrup in 80-100 parts methyl alcohol, and allowing to stand for a time; this is repeated until the cones are full of a dense crystallised mass, when the mother liquor is drained off and the loaves washed with methyl alcohol. The first crystallisations are obtained at a temperature of 30°, the final ones at 50°-60°. The methyl alcohol is recovered from the loaves and mother liquors by distillation in a vacuum.

Behr (*B.* 15, 1104; *G.P.* 21,101, 1882) obtained a pure commercial dextrose by taking the converted syrup concentrated normally to 82 p.c. solids containing at least 85 p.c. dextrose, adding some crystals of anhydrous dextrose, and maintaining the temperature at 30°-35°. After a short time an abundant crop of dextrose is produced, and is capable of being obtained in the dry state by treatment in a centrifugal apparatus (*v. SUGAR*). With purer converted products, *i.e.* containing a higher percentage of sugar, anhydrous dextrose crystallises out at 30°-35°. The first crystallisations are washed with methyl alcohol, this being recovered by distillation. According to the English patent the crystals from 87 p.c. sol. with a good conversion can be obtained sufficiently dense to be separated by a centrifugal machine. This product is found in the market.

Seyberlich and Frampebach (*E. P.* 8,000, July 1, 1883, *D. P. J.* 271, 512) convert starch by nitric acid, neutralise the converted liquid with chalk and make strongly alkaline with sodium carbonate, and evaporate the alkaline liquid to 33°-36°B. Dextrose separates on cooling in firm bold crystals, which can be freed from the mother liquor by a centrifugal machine.

For estimation of dextrose and mode of analysis of these products *v. SACHARIMETRY*.

*Glucose from cellulose.*—Wood, rags, paper, or, in fact, any kind of vegetable fibre, have also been proposed as materials for the preparation of dextrose, some mineral acid being the converting agent; but the change takes place with greater difficulty than with starch. Braconnet (*A.* 1820, 12, 172) observed that beech shavings were blackened and disintegrated when wetted with sulphuric acid; the chief product was almost completely soluble in water. The solution, after neutralising, filtering, and evaporating, yielded a white sugar resembling glucose from starch. Bayrhammer (*Berz. Jahres.* 1, 107)



made similar observations with regard to birch sawdust. There does not appear to be a product from this source in the market.

## O'S. &amp; II.

Further on this subject v. Gay-Lussac, A. Chim. 1820, 1; Döbereiner, Pneumatic Chem. Jena, 1822, 3, 48; Leuchs, Tech. Ency. Nürnberg, 1835, 3, 206; Pelouze, D. P. J. 151, 394; Pettenkofer, Gall's pract. Mitth. 1855, 1, 146 a. 87; article in Gibbs's Ann. 63, 357; D. P. J. 25, 81; Wagner's Jahresb. 1872, 597; Dauzville, B. 14, 385; Pochez, B. 15, 97; Le Myc and Peyster, E. P. 11, 407, August 18, 1884; Lesperment, S. C. J. 1884, 645; Clarke, E. P. 11, 557, August 22, 1884; Behr, E. P. 9, 797, July 5, 1881, and 1767, February 9, 1885.

**DHAURA.** A gum obtained from *Anogeissus latifolia*. It is extensively used in India in calico-printing; it occurs in clean straw-coloured elongated masses, sometimes honey-coloured or even brown from impurities. As an adhesive gum it is inferior in strength to gum arabic. In India, the reputation of this gum stands high with the calico-printers, especially of Lucknow, and it is probable it possesses some specific peculiarity justifying the preference, since it is used with certain dyestuffs, such as with haldi (*Circuma longa*), while gum arabic or 'babool' is used with madder (*Rubia cordifolia*) (Watts' Economic Products of India).

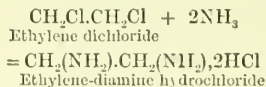
**DIALOGITE.** *Manganes carbonate v. MANGANESE.*

**DIAMIDO-BENZENES.** *Phenylene diamine v. DIAMINES.*

**DIAMIDO-TOLUENES.** *Toluylene-diamines v. DIAMINES.*

**DIAMINES.** *Diamido-compounds.* The diamines may be regarded as derived either from the hydro-carbons by the replacement of two hydrogen atoms by two amido-groups, or from two molecules of ammonia by the introduction of a dyad hydrocarbon radicle in the place of two atoms of hydrogen.

The diamines of the fatty series are obtained (1) by heating the alkylene dihaloids with ammonia:



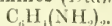
(Cloëz, J. 1853, 468). Secondary and tertiary diamines are formed at the same time. (2) By the reduction of the nitriles of dibasic acids with zinc and hydrochloric acid:



(Fairley, C. J. 1864, 362). The fatty diamines are only of theoretical interest.

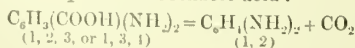
The diamines of the benzene series are obtained by the reduction of the dinitro-compounds or of the nitranilines.

**Phenylene-diamines (Diamido-benzenes)**



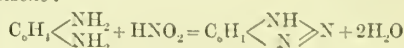
Theory predicts the existence of three of these, all of which are known.

1. *o*-Phenylene-diamine,  $\text{C}_6\text{H}_4(\text{NH}_2)_2$  (1, 2). First obtained by Griess by the distillation of *o*-*m*- and *m*-*p*-diamidobenzoic acid:

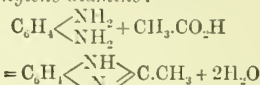


(J. pr. [2] 3, 143). By the reduction of *o*-nitranil-

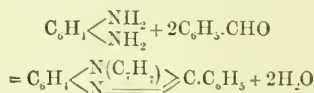
line  $\text{C}_6\text{H}_4(\text{NO}_2)(\text{NH}_2)$  (1, 2) (Zincke and Sintenis, B. 6, 123), or of *o*-dinitrobenzene  $\text{C}_6\text{H}_3(\text{NO}_2)_2$  (1, 2) (Rinne and Zincke, B. 7, 1374), with tin and hydrochloric acid.—Crystallises from water in laminae, melting at 102°. Boils at 252°. Readily soluble in water, alcohol, and ether. Diacid base: the sulphate  $2[\text{C}_6\text{H}_4(\text{NH}_2)_2].\text{H}_2\text{SO}_4.3\text{H}_2\text{O}$  forms nacreous laminae. Like many other ortho-compounds *o*-phenylene-diamine readily forms condensation products containing closed lateral chains. Thus with nitrous acid it yields *azimido-benzene*:



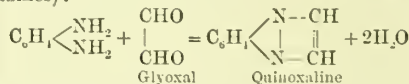
(Ladenburg, B. 9, 219; cf. Nölting and Abt, B. 20, 2299). When boiled with acetic acid it forms *ethenylphenylene-diamine*:



(Ladenburg, B. 8, 677); other acids convert it into similar compounds. It condenses with two molecules of benzaldehyde yielding *phenylbenzaldehyde* (benzyl-benzenylphenylene-diamine):

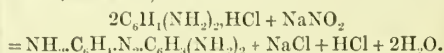


(Ladenburg and Engelbrecht, B. 11, 1653; cf. Hinsberg, B. 19, 2025). With  $\alpha$ -dicarbonyl-compounds it condenses to form quinoxalines (azines):



(Hinsberg, B. 17, 320; cf. Witt, B. 19, 915).

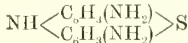
2. *m*-Phenylene-diamine,  $\text{C}_6\text{H}_4(\text{NH}_2)_2$  (1, 3). By reducing *m*-dinitrobenzene or *m*-nitraniline with iron filings and acetic acid (Hofmann, Pr. 11, 518; 12, 639), or with tin and hydrochloric acid (Gerdemann, Z. 1865, 61). By reducing either (1, 2, 4)- or (1, 2, 6)-dinitrobenzoic acid with tin and hydrochloric acid, the carboxyl-group being eliminated in the process (Zincke and Sintenis, B. 5, 791; Griess, B. 7, 1223). On a manufacturing scale it is prepared by reducing dinitrobenzene with iron turnings and hydrochloric acid.—Separates from its solutions as an oil which does not readily solidify unless brought in contact with a crystal of the base. Melts at 63°, and boils at 287°. Readily soluble in water. If sodium nitrite is added to a neutral solution of *m*-phenylene-diamine hydrochloride, triamido-azobenzene (*phenylene brown*, *Bismarck brown*, *resurine*) is formed:



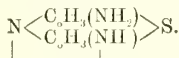
By means of this reaction the presence of 1 part of nitrous acid in 10,000,000 parts of water may be detected by the yellow colouration which is produced when a solution of *m*-phenylene-diamine in excess of sulphuric acid is added (Griess, B. 11, 624; Tiemann and Preusse, B. 11, 627). By the action of a diazobenzene salt on *m*-phenylene-diamine, *chrysoidine* (unsymme-

trical diamido-azobenzene) is produced. In the manufacture of phenylene-brown and chrysoidine the solution of crude *m*-phenylene-diamine hydrochloride obtained by the reduction of *m*-dinitrobenzene is employed, without first isolating the base. A violet colouring matter is obtained by heating *m*-phenylene-diamine with aniline hydrochloride to 190–200°, and a blue colouring matter by heating it with *m*-phenylene-diamine hydrochloride (Krause, B. 9, 835).

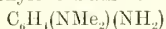
*p*-Phenylene-diamine  $C_6H_4(NH_2)_2$ . Obtained by reducing *p*-dinitrobenzene (Rinne and Zincke, B. 7, 871), or *p*-nitraniline (Hofmann, Pr. 12, 639), or amido-azobenzene (Martius and Griess, J. pr. 97, 263), with tin and hydrochloric acid, aniline being formed simultaneously in the case of amido-azobenzene. Along with diamido-diphenylamine by reducing aniline-black with tin and hydrochloric acid or with hydriodic acid and amorphous phosphorus (Nietzki, B. 11, 1097). By distilling (1, 2, 5)-diamidobenzoic acid (Griess, B. 5, 200).—Crystals, melting at 147°. Boils at 267°. Sublimes in leaflets. Readily soluble in water, alcohol, and ether. Yields on oxidation quinone. By heating it with sulphur to 150–180° it is converted into diamido-thiodiphenylamine (*leucothionine*, *Lauth's white*)



which, when oxidised with ferric chloride, yields thionine (*Lauth's violet*)

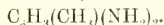


The latter colouring matter may also be obtained by the simultaneous oxidation of *p*-phenylene-diamine and sulphuretted hydrogen by ferric chloride in aqueous solution (Lauth, C. R. 82, 1441; Bl. 25, 422; Bernthsen, A. 236, 108). If dimethyl-*p*-phenylene-diamine



is substituted for *p*-phenylene-diamine in the foregoing reaction, tetramethylthionine (*methylene-blue*) is formed (v. METHYLENE-BLUE).

#### Tolylene-diamines (*Diamido-toluenes*)



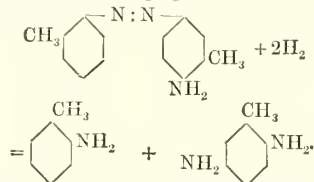
Six toluylene-diamines are theoretically possible, of which five have been prepared. Only two of these, however—*α*- and *γ*-toluylene-diamine—are of technical importance.

#### *α*-Tolylene-diamine $C_6H_3(CH_3)(NH_2)_2$ (1, 2, 4).

Obtained by the reduction of the corresponding dinitrotoluene (m.p. 71°) (Beilstein, A. 130, 242; 158, 350).—Needles, melting at 99°. Boils at 283–285°. Sparingly soluble in cold, readily soluble in boiling water, in alcohol, and in ether. Forms crystalline salts. As the two amido-groups in this compound are in the meta-position to one another, it is an analogue of *m*-phenylene-diamine, which it resembles in many of its reactions: thus *α*-tolylene-diamine may either wholly or in part replace the *m*-phenylene-diamine used in the manufacture of phenylene-brown, producing colouring matters the shade of which is redder than that of ordinary phenylene-brown.

*γ*-Tolylene-diamine  $C_6H_3(CH_3)(NH_2)_2$  (1, 2, 5) is obtained by the reduction of the corresponding *m*-nitro-*o*-toluidine  $C_6H_3(CH_3)(NH_2)(NO_2)$  (1, 2, 5)

with tin and hydrochloric acid (Beilstein and Kuhlberg, A. 158, 350; Ladenburg, B. 11, 1651). Formed along with *o*-toluidine when the amido-azotoluene prepared from *o*-toluidine is treated with the same reducing agent:



The two bases may be separated by fractional distillation (Nietzki, B. 10, 832). This reaction is utilised in preparing the mixture of *o*-toluidine and *γ*-tolylene-diamine which, after the addition of a second molecule of a monamine (either aniline or *o*- or *p*-toluidine), yields on oxidation saffranine. On a large scale the amido-azotoluene is reduced with iron turnings and hydrochloric acid.—Crystallises in colourless rosettes of tabular crystals melting at 65°. Boils about 280°. Readily soluble in water, alcohol, and ether, sparingly soluble in benzene. Yields on oxidation toluquinone  $C_6H_3(CH_3)_2O_2$ .

Similar diamines have been prepared from naphthalene and other hydrocarbons. F. R. J.

#### DIAMINE RED 3B v. AZO-COLOURING MATTERS.

**DIAMOND.** A natural form of carbon, crystallising in the cubic system. The commonest forms are the regular octahedron, the rhombic dodecahedron and the six-faced octahedron, all others being subordinate to these, and occurring generally in combination with them. The forms are to some extent characteristic of the locality: thus the octahedron is common in Cape stones, while Brazil yields rhombic dodecahedra and six-faced octahedra. It is notable that the faces of diamond crystals are often curved, and the six-faced octahedron, with its 48 rounded faces, may become almost a sphere. The curvature is in some cases due to a lamellar structure (*Schalenbildung*), the component lamellae regularly decreasing in size towards the centre of each face. In a glazier's diamond it is necessary that the cutting edge be cusped. The faces of diamond crystals are often striated parallel to the edges of the octahedron; they also exhibit impressions, or indentations, frequently of triangular shape, and it is noteworthy that similar impressions may be artificially developed, as shown by G. Rose, by subjecting diamonds to intense heat, without access of air (Ueber das Vorhalten d. Diamants u. Graphite bei d. Erhitzung, Monatsb. Berl. Ak. 1872, 516).

The frequent occurrence of triangular depressions on Cape diamonds has been adduced as proof of their exposure to subterranean heat.

Twin crystals of diamond are not uncommon; and flat triangular hemitropes, splitting easily along the plane of union, are known to the Amsterdam workers as *Nahtsteine*. (On the crystallisation of diamond, v. Sadebeck, Monatsb. Berl. Ak. 1876, 578; Hirschwald, Zeits. f. Krystal. i. 1877, 212; and Weiss, N. Jahrb. f. Min. 1880, ii. 12.)

The cleavage of the diamond is perfect parallel to the faces of the octahedron. The

cutter frequently takes advantage of this cleavage in removing portions disfigured by flaws, and in dressing rough stones to be cut as brilliants. Notwithstanding the ancient belief that a true diamond could bear the blow of a hammer, it is rather a brittle stone, not only splitting along the cleavage-planes, but breaking elsewhere with a conehoidal fracture. The hardness of the diamond is indicated as 10 on the mineralogical scale, but it is so greatly superior to that of any other mineral that this is merely an arbitrary expression. Crystals from different localities vary considerably in degree of hardness: thus, lapidaries assert that Indian diamonds are harder than the Brazilian, and these, again, harder than South African stones. The hardness may vary on different faces of a single crystal, and even in different directions on the same face. The sp.gr. of diamond ranges from 3.509 to 3.550, the mean being about 3.514 (Schrötter). Baumhauer determined the density of a nearly colourless Cape diamond to be 3.51812.

Diamonds vary greatly in colour. The purest, or stones of the 'first water,' are practically colourless; while certain stones, known as 'blue whites,' incline to a faint bluish tint; the best example of this type being the Porter-Rhodes diamond—a stone of 150 carats, found at the Cape in 1880. Most of the 'off-coloured' stones present yellow or brown tints; the colour cannot be discharged by heat, but yellow diamonds have sometimes been washed with dilute violet ink, whereby the tint is superficially neutralised. The dark colour of some diamonds has been doubtfully referred to the presence of crowds of minute internal cavities, revealed by microscopic examination (Brewster).

While off-coloured stones are of comparatively small value, those which possess a pronounced and pleasing colour are highly prized as 'fancy stones.' A deep-red colour is the rarest. The famous Hope diamond is a fine sapphire-tinted stone of  $44\frac{1}{2}$  carats; while the Saxon diamond, in the Grüne Gewölbe in Dresden, presents a delicate green colour.

The index of refraction is higher in diamond than in any other known transparent substance. According to Des Cloiseaux, it is 2.414 for red rays, and 2.428 for green. It was the high refraction of diamond that led Newton to conjecture that it might be 'an unctuous substance coagulated.' The character of the lustre is known as adamantine. Much of the brilliancy of the polished stone is due to its small critical angle ( $24^{\circ} 24'$ ), since a very large proportion of the rays entering the diamond must be necessarily returned by total reflection. The coefficient of dispersion is higher than in most transparent bodies; it is given by Jannettaz as 0.044. Examined in polarised light many diamonds exhibit an anomalous behaviour, apparently due to internal strain. Brewster, who supposed that the diamond might have been originally a vegetable gum, explained the depolarising action which certain diamonds display between crossed nicols as the result of tension caused by included bodies. Chatrion has found a crystal of iron pyrites in a Brazilian diamond.

After exposure to solar light, the diamond becomes highly phosphorescent, and different faces of the same crystal may emit rays of dif-

ferent colours. Submitted to molecular discharge in Crookes's exhausted tubes, the diamond glows with great brilliancy. On exposure to the heat of the electric arc, it swells up, cracks on the surface, and becomes coated with a substance resembling graphite. In its ordinary state the diamond does not conduct electricity, but the coke-like mass obtained by exposure to the arc is a good conductor.

The study of the action of heat upon the diamond, with and without the presence of air, gave the earliest clue to its chemical composition. The famous experiment of the Florentine academicians, Averani and Targioni, made in 1694, at the instance of the Grand Duke Cosmo III., showed that it could be volatilised by heat. In 1751 the Emperor Francis I. caused a quantity of diamonds and rubies to be placed in a crucible and exposed to great heat, when it was found that the diamonds disappeared, while the rubies were fixed. Darcet afterwards showed that though the diamonds vanished if heated in an open crucible, they remained unaltered if air were completely excluded. In 1772 Lavoisier demonstrated that the diamond is truly combustible, and yields carbon dioxide; and it was subsequently shown by Smithson Tennant that equal weights of charcoal and of diamond gave equal weights of this gas. By heating diamond with iron, Guyton de Morveau obtained steel, and thus indirectly showed the probable composition of the mineral. The experiments of Davy, in 1816, proved that the diamond was practically pure carbon: a result confirmed by the refined investigations in determining the atomic weight of carbon by Dumas and Stas, and subsequently by Roscoe and by Friedel. The behaviour of diamonds when exposed to high temperatures in various gaseous media has been studied by M. Morren (C. R. 70, 990).

On the combustion of the diamond there remains a quantity of a colourless or reddish ash, varying from one five-hundredth to one two-thousandth of the original weight of the mineral. Microscopic examination of this delicate spongy ash led Göppert, Petzholdt, and others to believe that it shows traces of cellular tissue, suggestive of a vegetable origin.

Various hypotheses have been advanced to explain the origin of the diamond, but these have rarely been subjected to experimental verification or disproof. Liebig suggested the decomposition of liquid hydrocarbons, while Chancourtois and others have resorted to hydrocarbonaceous vapours. Carvell Lewis, basing his opinion on the occurrence of diamonds in South Africa, derived the mineral from the action of eruptive rocks on carbonaceous shales (Geol. Mag. 1887, 22). As many of the minerals associated with the diamond in Brazil have been formed artificially by the decomposition of chlorides at a high temperature, it has been suggested by A. Favre that the decomposition of chloride of carbon may have yielded the diamond. Gannal attempted to obtain it from carbon disulphide. Reviewing the geological conditions under which diamonds occur in various parts of the world, it is seen that these are so different in different localities as to suggest that the natural process of diamond-making has not been uniform. Thus, in Brazil



and in India the diamond appears to be associated with acid rocks, while in South Africa it occurs in a highly basic rock, resembling an altered peridotite.

The most ancient diamond mines are those of India, whence the precious stone has been obtained from remote antiquity. The Indian diamonds are found in river gravels, and in superficial deposits scattered over the country, while occasionally they occur in sandstones of the Vindhyan formation, but these probably do not represent the original matrix. In 1884 Chaper announced the discovery of the diamond in a pink pegmatite, at Bellary in Madras (C. R. 98, 1884, 113), but this seems doubtful. Diamonds have been worked in three extensive districts in India. The mines of the most southern group are partly in the Madras Presidency and partly in the territory of the Nizam, the most famous workings having been those on the Kistna and Godavery rivers, improperly known as the mines of Golconda. The 'Golconda' district yielded most of the great historical diamonds, such as the Koh-i-nur, the Regent, and the Great Mogul; and workings have recently been reopened at Partaal (W. Morgans' Report, 1889). Diamonds also occur in the districts of Kudapah, Bellary, and Karnul, but most of the mines are now abandoned. In 1881 a diamond of irregular shape, weighing  $67\frac{3}{4}$  carats, was found near Wajra Karur, in the Bellary district, and yielded a fine brilliant of  $24\frac{1}{2}$  carats, known as the 'Gor-do-Norr' (Mallet). Another group of diamond localities is situated in the Central Provinces: at Sambalpur on the Mahanadi river, and at Wairagarh. The mineral is also found in Chuta Nagpur in Bengal; while further to the north is a third group of mines, including those of Panna in Bundelkhand, still worked on a limited scale. (For Indian diamonds, *v.* Manual of the Geol. of India; vol. 3 Economic Geology, by V. Ball, 1881, and vol. 4 'Mineralogy,' by F. R. Mallet, 1887.)

Although the sands of many of the rivers of Brazil had been long worked for gold, it was not until 1727 that the occurrence of diamonds in association with the precious metal was observed. The distribution of the diamond is extensive, occurring locally in the provinces of Minas Geraes, Goyaz, Bahia, Matto Grosso, Parana, and San Paulo. The best-known locality is Diamantina, formerly called Tejuco, in Minas Geraes. The diamond occurs in gravels mixed with clay, and forming a loose conglomerate known as *cascalho*; while if the quartz pebbles are less rolled, as in the plateau gravels, it is termed *gorgulho*. The diamond is said to have been found in a metamorphic sandstone called *itacolumite*, and it is asserted that where itacolumite is not present the neighbouring gravels never bear diamonds. In the Diamantina region the original matrix seems to be in veins of quartz and clayey matter, carrying iron pyrites and tourmaline, and traversing a series of hydro-mica schists and itabirites, with itacolumite. In the sands and gravels the diamond is associated with rutile, anatase, brookite, magnetite, hematite, ilmenite, &c. (For Brazilian diamonds, *v.* papers by Orville Derby in Am. J. [3] 24, 1882, 34; and Goreeix in C. R. 113, 1881, 981.)

It appears that the occurrence of diamonds in South Africa was known certainly as far back as the middle of the last century, yet it was not until 1867 that attention was re-called to this forgotten discovery. At that time the child of a Dutch farmer near Hopetown picked up among the pebbles of the Vaal river a diamond weighing  $21\frac{3}{16}$  carats. Search in the neighbourhood soon led to other discoveries, one of the earliest being that of a stone of  $83\frac{1}{2}$  carats, which came to be known, when cut, as the Star of South Africa, or the Dudley diamond. The earliest workings were 'river diggings,' in the gravels of the Vaal and some of its tributaries, especially near Pneil and Klipdrift. The largest diamond obtained from the river diggings was the 'Stewart,' a stone weighing  $288\frac{1}{2}$  carats, found in 1872 at Waldeck's Plant, on the Vaal. On the discovery of diamonds in the soil at Du Toit's Pan, most of the river diggings were abandoned in favour of what were called 'dry diggings.' The principal mines at present worked are those of Kimberley, De Beer's, Du Toit's, and Bultfontein, all within a limited area in the British territory of Griqualand West; but diamonds are also worked at Jagersfontein, in the Orange Free State—a locality which yields diamonds of exceptional purity, known in the market as 'glassies.'

The South African diamonds occur mostly in a serpentinous breccia, filling vertical pipes, which, piercing the surrounding rocks, rise to the surface, where their presence was originally marked by little hills or *kopjes*. A reddish sandy soil occupied the surface, beneath which occurred a deposit of calcareous tufa; this passed downwards into the 'yellow earth,' which finally merged into the so-called 'blue ground.' The yellowish material was simply the upper part of the blue earth more or less altered by surface agencies.

It is now generally believed that the pipes, or chimneys, are ancient volcanic ducts, through which the diamond-bearing material has been brought up from some deep-seated source. The pipes traverse black and reddish shales of the Karoo formation, believed to be of triassic age, associated with sheets of basaltic rocks, and resting upon a granite base. The edges of the schist are slightly upturned, as if by pressure from below, but they do not show signs of fusion or other alteration suggestive of a high temperature. The walls of the chimneys are smooth, or vertically striated, and between the walls and the contents of the pipes there are occasional hollows lined with crystals of calcite, and sometimes yielding explosive gases, apparently derived from the carbonaceous shales.

The materials filling the pipes consist of fragments of the schists and other neighbouring rocks, usually sharp at the edges and not fused, cemented into a hard breccia by a greenish serpentinous material, chiefly a hydrated ferromagnesian silicate, which is probably an altered enstatite or bronzite (for analysis, *v.* Maskelyne and Flight, Quart. Journ. Geol. Soc. 30, 1874, 406). The embedded diamonds are associated with garnets (pyrope), sometimes known in trade as 'South African rubies'; with green salite, and a peculiar mica, named by Maskelyne *Vaalite*, which appears to be an altered biotite. Ilmenite

is present, and is sometimes mistaken for carbonado or black diamond. Among the other associates of the diamond are iron pyrites, magnetite, and zircon. It is notable that the diamonds are often fragmentary, and neighbouring fragments do not correspond, thus suggesting that fracture occurred at some deep-seated point. Much discussion has arisen as to the original character of the blue rock; but most geologists now regard it as an altered volcanic product which was probably brought up in a pasty condition, not at a very high temperature, but perhaps rather like the materials of a mud volcano. Carvell Lewis described the rock as an altered peridotite under the name of *Kimberlite*, and concluded that the matrix of the diamond in many parts of the world was probably serpentine, resulting from the alteration of an erupted peridotite (Rep. Brit. Ass. 1887 meeting, 720).

Until recently the diamond mines of South Africa were worked as open quarries; but, serious difficulty having arisen from falls of the surrounding rock, known locally as 'reef,' systematic underground mining has been introduced. Outside the pipe a shaft is sunk, and galleries are thence driven into the diamond ground. The blue earth, when first hauled up, is extremely hard, but by exposure to air and water it is readily disintegrated, and the diamonds are then separated by washing. (For account of South African diamonds, *v. Moulle* in Ann. d. Mines [8] 7, 1885, 193; *Boutan* in Ency. Ch. 1886.)

Borneo has yielded diamonds from remote antiquity. They occur in alluvial clays, river sands, and drift gravels; occasionally, too, they have been found in an eocene conglomerate, but this is a derived rock, and the original matrix is unknown. The deposits are worked in a primitive manner by the Dyaks, and to a limited extent by Chinese; of late, however, French engineers have commenced systematic working at Tjempaka, in South Borneo. The chief localities for diamonds are Landak in the west, Knsan in the east, Tanah-laut in the south, and the Serawak river in the north. The Sultan of Matan has long been reputed to possess the largest Borneo diamond—an uncut stone weighing 367 carats; but it was shown a few years ago that this stone is merely rock crystal. The Sultan of Martapura, in Tanah-laut, possesses a diamond of 77 carats found at Gunong Lawak. The 'Star of Serawak' is a Landak stone of 70 carats. The production of diamonds in Borneo has greatly fallen off of late years, especially through the introduction of Cape stones. (*V. Posewitz's Borneo*, Berlin, 1889, 293.)

In Australia diamonds are known to occur at numerous localities, especially in New South Wales, but the stones are invariably small. They have been worked commercially in drift gravels on the Cudgegong river, near Mudgee, and at Bingera and Inverell in New South Wales (*v. Liversidge*, Min. of New South Wales, 1888, 116). Diamonds have also been found, though but rarely, near Echunga in South Australia, and at Bechworth and elsewhere in Victoria.

Numerous localities for diamonds are known in the United States. They occur in association with gold in New Carolina, in Georgia, and in Butte Co., California; while they are found with platinum in Oregon. A remarkable crystal

was brought to light a few years ago at Manchester, opposite Richmond, in Virginia, and after cutting became known as the On-i-nur, or 'sun of light.' (For diamonds in United States, *v. G. F. Kunz*, in successive volumes of Mineral Resources, by United States Geolog. Survey.)

It was announced in 1829 that diamonds had been found in the Ural Mountains; but though subsequent discoveries were reported, the evidence seems to need confirmation. The same remark applies to the reputed discoveries near Constantine in Algeria. It appears, however, that credence may be given to the discovery of a crystal of diamond, in 1870, in the garnetiferous sands of Blaskowitz in Bohemia.

It has lately been shown that the diamond is to be included in the list of extra-telluric minerals. On September 22, 1886, three meteorites fell near Novo Urei, in the Government of Penza, South East Russia. One of these, examined by MM. Jeroifeff and Latchinoff, was found to contain carbonaceous matter, partly as amorphous carbon, and partly diamantoid; the latter, forming about 1 p.c. of the stone, occurred in microscopic grains, believed to be carbonado (C. R. 106, 1888, 1679).

Carbonado is the name given to a black or dark-grey form of diamond, which was discovered in 1842 in the province of Bahia in Brazil, and is at present known to occur only in Brazil and Borneo. It is generally found in irregular or rounded masses, occasionally with indistinct crystalline form, and presenting on fracture a compact, granular or cellular structure. Its sp.gr. is less than that of true diamond, being in some cases as low as 3.01; nor is it so pure as crystallised diamond, some specimens yielding on combustion as much as 2 p.c. of ash. Notwithstanding its impurity, it exceeds in hardness any other form of diamond; and this has led to its extensive use in the arts. In the diamond-mounted rock-drills of Leschot and Beaumont, pieces of carbonado are firmly embedded in the inner and outer edges of the steel tube which forms the head of the drill; and so valuable is the carbonado that a single crown, with its setting, may be worth 2,000*l.* The carbonado is also used in tools for dressing mill-stones and emery-wheels.

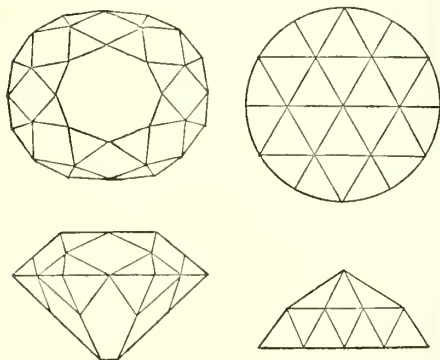
Another variety of diamond used in the arts is known as *bort*. Mineralogists recognise under this name an impure translucent variety, not crystallised, but presenting a crystalline structure, and generally occurring in small concretionary masses of dark-grey or black colour, with a rugose exterior. It is slightly less dense than crystallised diamond, its sp.gr. not exceeding 3.505; but it is extremely hard, though excelled in this respect by carbonado. True bort occurs in most diamond-bearing districts, but much of the bort of commerce is merely coarse diamond, too much flawed or splintered to be used by the jeweller. The bort is crushed in a steel mortar, and the powder is extensively employed by lapidaries and others as a powerful abrading agent.

The art of cutting and polishing the diamond is generally attributed to Louis de Berquem, of Bruges, who is said to have first practised it about 1456. The forms into which diamonds are cut at the present day are known as the *brilliant* and the *rose*. The former may be

roughly described as consisting of two truncated and faceted cones, applied base to base: the upper part, or *crown*, is more truncated than the lower part; the edge of union between the two parts is termed the *girdle*, while the broad flat upper face is the *table*, and the small lower plane the *culet*. The rose has a flat base, from which rises a hemispherical dome covered with triangular facets (*v. figs. below*).

In cutting a diamond, the first step is usually to reduce it by cleavage to a convenient shape. To cleave the mineral, the operator embeds it in a cement of resin and brick-dust, carried at the end of a small wooden baton. The cement having been warmed, the diamond is fixed in such a position that only the part to be split is exposed. Along the direction of cleavage, a furrow is cut by means of another diamond: into this groove a thin steel blade is inserted, and by a sharp blow, skilfully delivered on the blade, the cleavage is effected.

After cleavage the stone is cut, or rather rubbed, into the required shape. Two diamonds, each embedded in cement, with only a small surface exposed, are patiently rubbed together until by mutual attrition two plane surfaces are formed. The operator wears stout gloves to protect the fingers, and takes care that every particle of dust resulting from the friction is carefully preserved. When the faces have been formed by this rubbing, or 'bruting,' they require to be polished on the mill. The diamond is embedded in a ball of fusible metal, carried in a hemispherical cup at the end of an arm, which being loaded with movable weights enables the manipulator to adjust the pressure on the wheel. The wheel is a circular iron disc, about 10 inches in diameter, rotating in a horizontal plane at the rate of about 2,000 or 3,000 revolutions per minute. The movement is usually effected by steam power, but Sir H. Bessemer has introduced electricity at the works of Ford and Wright in Clerkenwell. The rotating discs are fed with diamond-dust and olive oil.



The diamond-cutting industry has for centuries been centred in Amsterdam, where it is mainly in the hands of Jews; but mills have also been established at Antwerp, and, of late years, at Hanau, near Frankfurt; in Switzerland, and in London. The trade has received a great impetus in recent years by the enormous output

of the South African mines, which now practically supply the world.

The following table gives the weight and value of the diamonds produced by the mines of British South Africa during the year 1888 (Sawyer):—

	Carats	£
Kimberley	1,332,809	1,270,873
De Beer's	1,003,406½	935,444
Du Toit's	569,013½	758,464
Bultfontein	659,887½	642,763
Small mines	657¾	668
	3,565,774½	£3,608,212

[For recent information on the diamond *v.* A. H. Church, *Precious Stones*, London, 1883; E. W. Streeter, *Precious Stones*, 4th ed., London, 1884; M. E. Boutan, *Diamant* in *Fremy's Ency. Ch.*, Paris, 1886; H. Jacobs and N. Chatrian, *Le Diamant*, Paris, 1884; E. Jannettaz and others, *Diamant et Pierres Précieuses*, 2nd ed., Paris, 1881; P. Groth, *Grundriss der Edelsteinkunde*, Leipzig, 1887.] F. W. R.

**DIANA.** The alchemistic name for silver.

**DIANTHINE** *v.* **TRIPHENYLMETHANE COLOURING MATTERS.**

**DIASPORE.** Native monohydrate of alumina  $Al_2O_3 \cdot H_2O$  (*v.* **ALUMINIUM**).

**DIASTASE**, the unorganised ferment under the influence of which starch is converted into sugar.

*Occurrence.*—It is found in germinated barley (Payen a. Persoz, A. C. [2] 53, 72; 56, 237; 60, 441; 61, 351; Guérin-Varry, A. C. [2] 57, 108; 60, 22; 61, 22; Dubrunfaut, *Les Mondes*, 16, 317), in the leaves of most plants, and in many germinating seeds (Brasse, C. R. 99, 878); diastatic action is fairly well distributed in the vegetable kingdom (Gorup-Besanez, N. Rep. P. 25, 28; B. 7, 1478; S. 1510), and the ferment is present in horse chestnut at all stages of its growth, in ungerminated barley, and in the hilum and embryo of maize, but beech does not contain it (Kranich, *Bied. Centr.* 1879, 120). Saliva possesses diastatic action (Mihali Chin. apléphysiol. f. Paris, 1856, 28; v. Meiring. *Ztschr. Ph. Chem.* 5, 185). Magendie (C. R. 23, 189) observed that starch paste, mixed with fresh blood serum and kept at 40°, was liquefied in a few minutes, and dextrin and sugar could be detected at the end of a quarter of an hour. According to Bouchardat (A. Ch. [3] 14, 61) putrid flesh, yeast, gastric juice, and animal membrane transform starch; hence diastase is present in these substances. The microzymes of barley exhibit diastatic action (Béchamp, C. R. 83, 358). It is developed by allowing the spores of a fungus to grow on steamed rice (Atkinson, *Pr.* 10, 203). Marciano (C. R. 95, 856) maintains that diastatic action is a function of bacteria, which are always developed during the germination of seeds. Barley-extract possesses transforming power, which is diminished by the growth of schizomycetes, but considerably increased by the growth of saccharomyces (Brown and Heron, C. J. 35, 653). Diastase is widely distributed in animals and plants (Mulder, *Chem. des Biers*, 225), and in both it is frequently accompanied by invertase; the latter is due to microphytes (Bourguelot, *J. Pharm.* [5] 11, 367). The diastase of wheat is the same as that of



barley, and the quantity in the former is as great as in the latter (Lintner, J. pr. 36, 481).

*Preparation.*—The preparation of diastase in the pure state has not yet been satisfactorily accomplished. A highly active preparation is obtained from low-dried barley malt, as follows (O'Sullivan, C. J. 45, 2). Two or three kilos. of finely-ground pale barley malt are taken, sufficient water added to completely saturate it, and, when saturated, to slightly cover it. When this mixture has stood 3 or 4 hours, as much of the solution as possible is pressed out by means of a filter press. If the liquid is not clear it must be filtered. To the clear solution, alcohol sp.gr. '830 is added as long as a flocculent precipitate forms, the addition of alcohol being discontinued as soon as the supernatant liquid becomes opalescent or milky. The precipitate is washed with alcohol sp.gr. '86–'88, dehydrated with absolute alcohol, pressed between cloth to free it as much as possible from that liquid, and dried *in vacuo* over sulphuric acid until the weight becomes constant. Payen heated the malt extract to 75°, to coagulate albumen, before precipitating the diastase; it has since been shown (O'Sullivan, C. J. 1876, 2, 125), and confirmed by others, that the action of diastase is altered by heating. Wittich extracted green barley malt with glycerol, pressed the extract, and precipitated with absolute alcohol and ether. Zulkowsky (W. A. B. 77 [2] 647) first extracts malt with strong alcohol, then with glycerol, which he presses out after 8 or 12 days, and precipitates the diastase from the diluted and filtered glycerolic extract by absolute alcohol and ether. Lintner (J. pr. 34, 378) says that the method does not give so good a yield as is obtained by saturating malt-extract with sodium chloride, and washing the precipitate with ether and alcohol. He, however, recommends the following mode of preparation: one part green barley malt or flour of air-dried malt is treated with 2–4 parts of dilute spirit (20 p.c. alcohol) for 24 hours or more, the extract is pressed from the insoluble matter, and precipitated by adding 2½ times its volume of absolute alcohol. The precipitate is then dehydrated by treatment with absolute alcohol and ether, and dried in a vacuum over sulphuric acid. Brasse (C. R. 100, 454) prepared diastase from various seeds and plants by macerating the broken parts with water for 24 hours, adding to the pressed and, if necessary, filtered extract 1½ times its volume of alcohol (sp.gr. '82–'83), allowing the precipitate to subside, and adding to the filtrate as much more alcohol. The precipitate thus obtained contained diastase.

No matter how active these products may be, it is obvious that they are not pure bodies. Lintner says his preparation contained 16 p.c. ash. Loew (Pflüger's Archiv, 1882, 203) obtained a highly active purified diastase by treating the crude body with lead acetate, separating the lead with hydrogen sulphide, and precipitating with alcohol. Lintner maintains that the precipitate with lead acetate does not contain a fourth of the active diastase of the crude body. He attempted to obtain a pure body by fractional precipitation with alcohol and selection of the most active fraction. This does not eliminate the ash, for which purpose he submitted the

preparation to dialysis. He thus reduces the amount of ash to 4.79 p.c. Loew (B. 20, 58) does not agree with Lintner, and considers his want of success with the lead acetate treatment due to secondary causes.

*Composition.*—The following analyses of the purified preparation are given:

Constituents	Gorup-Besanez. Preparation from vetch	Lintner. Malt of barley and wheat	Zulkowsky. Barley malt	Kranch
Carbon .	—	46.66 <sup>1</sup>	47.57	45.68
Hydrogen .	—	7.35	6.49	4.90
Nitrogen .	4.3	10.42	5.14	4.57
Sulphur .	—	1.12	} 37.64	36.77
Oxygen .	—	—		
Ash .	7.76	—	3.16	6.08

The ash contains potassium, calcium, and magnesium phosphates, with a trace of sulphates. Payen states that the freer the body is from nitrogen the more active it is. It seems, however, that the more we learn of the attempts to isolate this body the clearer it is that the idea of Mulder, that it is not a definite compound, is true.

*Properties.*—The preparations, obtained as described above, are, if carefully prepared, white, amorphous, and friable, easily soluble in water; but if allowed to dry without being dehydrated with absolute alcohol they are horny, and not easily penetrated by water. The solution is not coagulated by heat, or heat and acids; it is optically active, being highly levorotatory (author), neutral, and devoid of taste. The chief property of diastase is its action on gelatinised starch. Ungelatinised starch is not acted on by diastase (O'Sullivan, C. J. 1876, 2, 133), confirmed by Brown and Heron (C. J. 35, 621). The contrary is stated to be the fact by Kjeldahl (Mdl. f. Cbg. Lab. 2, 1879). It is probable that diastase attacks certain kinds of starch and starch granules at certain stages of growth in the cold. Diastase dissolves gelatinised starch at all temperatures up to 75°–76°, at or about which temperature the activity is destroyed. When starch paste is dissolved by sufficient diastase at 63°, one-third is converted into dextrin and two-thirds into maltose (O'Sullivan, *l.c.*); confirmed by Kjeldahl (*l.c.*). Brown and Heron (*l.c.*) give other proportions. Other bodies besides dextrin and maltose are formed when starch is dissolved by diastase (*v. Starch*). The final product of the action is maltose (O'Sullivan, C. J. [2] 10, 581), but it is probable that certain forms of diastase convert maltose into dextrose (O'Sullivan, C. J. 1876, 2, 139; Atkinson, Pr. 10, 203). The activity is affected by heat; weakening begins early, but it is slow in proportion to the rise of temperature until 63°, or thereabouts, is reached, after which there is a rapid loss of power to 75°–76°, a short exposure in solution to this temperature completely destroying the power. Diastase resists a high temperature better in presence of starch than by itself. It converts starch at 17.5° without loss of activity, but the maximum effect from

<sup>1</sup> The body burned contained 4.79 p.c. ash; the percentages are calculated on the body free from ash.

a given weight of diastase is obtained at 50° (Lintner). When deprived completely of its water over sulphuric acid at the ordinary temperature it may be heated to 100° without suffering much loss of power. Dilute solutions become quickly acid and lose their power, but concentrated ones are very stable, opposing the growth of micro-organisms for a considerable time and retaining their activity. Preparations, even in a moderately dry state, are subject to diminution of transforming power. The activity of diastase is destroyed by nitric, sulphuric, hydrochloric, phosphoric, oxalic, tartaric, or citric acids, potash, soda, lime, copper sulphate and acetate, mercury bichloride, silver nitrate, alum, ferric sulphate; retarded by formic acids, arsenious acid, magnesia, ammonia, and alkaline carbonates, and in a less degree by acetic acid, hydrocyanic acid, strychnine, quinine, morphine, and their salts. Essential oils, creosote, alcohol, and ether exert no retarding influence (Boucharlat). One part sodium hydroxide in 500,000 parts neutral starch paste reduces the activity of diastase by 26 p.c.; further addition of alkali destroys the action completely; .003 p.c. sulphuric acid diminishes the action (Duggan, Am. J. 306). Free acids and alkalis, as well as salts of the heavy metals, destroy the action of diastase. Solutions of .4 p.c. alkaline chlorides or calcium chloride have no effect, but solutions containing 4-8 p.c. increase the activity (Lintner, J. pr. 36, 481). Formaldehyde is highly destructive of diastase; .15 gram hydroxylamine destroys 1 gram diastase in 24 hours, but the same quantity does not effect 10 grams. Nitrous acid also destroys the action (Loew, J. pr. 37, 101). Carbonic acid has no influence on its action on some kinds of starch, nor does pressure affect the activity (Baswitz, B. 12, 1827; Bert, C. R. 80, 1579). Hydrochloric acid, or pure gastric juice, destroys the transforming power (Defresne, C. R. 89, 1070). Very dilute hydrochloric acid increases the activity (Kjeldahl).

The purified diastase of Lintner gives almost all the reactions of the albumins, but not those of the peptones. It gives in a marked manner a reaction given by no other protein body, viz., with *guaiacum* tincture and hydrogen dioxide (the tincture gives better results than the aqueous solution as recommended by Schönbein), a blue colour, which is soluble in ether, benzene, chloroform, carbon disulphide, and may be extracted from the solution by those solvents. Rennet, saliva, pepsin, and invertin give no reaction under like conditions. The reaction does not take place when the diastase solution is boiled for a short time, or after the addition of alkalis or acids, in fact under the condition in which the fermentative action is destroyed. The slightest trace of diastase can be detected by the *guaiacum* reaction, for example in the steep-water of barley, maize, wheat, &c. On submitting diastase solutions to filtration through a porous battery cell, diastase does not pass through (Brown and Heron).

*Estimation of diastatic power.*—Diastase not having been obtained in a pure state from any source, it is not possible to estimate it absolutely. The relative activity of materials or preparations exhibiting the fermentative activity

can, however, be estimated with a fair amount of accuracy. If, for example, it is required to determine the relative diastatic power of two samples of malt, it is only necessary to weigh out 10 grams of each finely ground, add 100 c.c. cold water, and stir the mixture occasionally for 6-8 hours. A clear filtrate is obtained from each and 10 c.c. of it are allowed to act for 5 minutes at 60°-63° on 100 c.c. starch paste containing 5 grams purified air-dried potato starch. The solutions are then rapidly boiled, and evaporated to 100 c.c. A determination of the specific gravity and optical activity will give the percentage of dextrin and maltose (*v. Saccharimetry*) allowance being made for the optical activity and specific gravity of the malt extract employed. One of the samples is found to contain one-third dextrin and two-thirds maltose or quantities approximating to these, in the other the proportion of maltose is higher; in this case 9 c.c. of the malt extract are allowed to act on the same amount of starch paste. On examining the products the maltose still exceeds 66 p.c. of the transformed bodies. 8 c.c. are then tried; this does not yield 66 p.c. maltose. 8.5 c.c. are tried; this yields the required quantity of maltose. 10 c.c. of the first and 8.5 c.c. of the second are then made to act on two separate 100 c.c. of the standard starch paste at the temperature given and the digestion is continued for 30-40 minutes. If the proportion of maltose is about 66 p.c. in each, the c.c. represent the relative activities of the malts, if not, the one showing the most maltose is the most active and a further experiment should be made with a less quantity. In this way very close relative quantities can be arrived at. These results may be expressed thus: the diastatic power of the first malt is 10, of the second, 8.5; *i.e.* 10 grams of the first malt exhibit only as much diastatic power as 8.5 of the other. Further on this subject see Kjeldahl (D. P. J. 235, 379), and Lintner (Bied. Centr. 1885, 855). O'S.

**DIDYMIUM** *v.* CERIUM METALS.

**DICETYLIC ACID** *v.* FATTY ACIDS.

**DIETHYL ACETIC ACID.** *Pseudo-caproic acid v. FATTY ACID.*

**DIGALLIC ACID** *v.* HYDROXY-ACIDS.

**DIGESTER** *v.* AUTOClave.

**DIGITALIS.** *Foxglove.* (*Digitale*, Fr.; *Fin-gerhut*, Ger.) The foxglove, or *Digitalis purpurea* (Linn.), is well known for its elegant appearance and beautiful purple-crimson flowers throughout the British Islands and most parts of Europe (*cf.* Woodville, Med. Bot. 24; Benth. A. T. 195). Foxglove is a powerful arterial sedative, reducing the force and frequency of the heart's action, and has been in use in medicine since the sixteenth century. The leaves are generally employed, but the seed possesses a like activity. For time of gathering see Brit. Pharm. 1885; Schneider (Bl. Ph. 1870, 164); Nativelle (J. Ph. [4] 20, 81).

Numerous attempts have been made to isolate the constituent or constituents upon which the physiological action of digitalis depends, and more or less definite substances have been from time to time announced, the relation of which to one another is at the present day a matter of uncertainty. A *résumé* of the early work is given by Pereira (Mat. Med. 1850, 2,

1386). Active extractives were obtained, and variously named *digitaline*, *picrin*, or *scaptin*, in addition to other constituents common to plants.

Homolle was, however, the first investigator to prepare a fairly definite physiologically active substance from foxglove leaves. To obtain the *digitaline* of Homolle, a dried alcoholic extract of the leaves is exhausted with acetic acid and water, the solution purified by treatment with animal charcoal, and the soluble acetate converted into insoluble tannate, from which the digitaline is set free by the action of oxide of lead. The crude product is freed from inactive constituents by washing with ether. The digitaline thus obtained is exceedingly bitter, and irritating to the nasal membranes. It is white, inodorous, and imperfectly crystalline. It is insoluble in water and ether, but dissolves in alcohol. In sulphuric acid it dissolves brown to crimson after standing a few days, and in hydrochloric acid yellow to green. This is the digitalin which has from time to time found a place in the pharmacopœias (Homolle, J. Ph. [3] 7, 57; Henry, J. Ph. [3] 7, 460; Homolle and Quevenne, Mémoires sur le Digitaline, Paris, 1851). It possesses the physiological activity of digitalis (Homolle; Bourchardat and Sandras, Ann. Thérap. 1845, 60). The *digitaline* of Delffs (N. J. P. 9, 26), a further purified form of Homolle's product, gave analytical numbers corresponding with the formula  $C_{22}H_{34}O_{10}$ .

Waltz (Jahrb. pr. Pharm. 14, 20; 21, 29; 24, 86; Geh. Traité, 4, 286; N. J. P. 6, 332; 9, 302; 10, 319) by treating Homolle's digitaline with ether extracts a substance *digitalacrin*, which, in its turn, he separated into *digitaloic acid*  $C_{17}H_{22}O_8$ , insoluble in water, but soluble in ether and alcohol, and digitalin fat or *digitaloin*, in crystalline scales (cf. Delffs, J. 1858, 528; Goerz, J. 1873, 816). From the residue after treatment with ether Waltz extracts with water a yellow amorphous mass, physiologically active in the highest degree. This is *digitasolin* or *digitaletin*, or *digitalin* of Waltz. It is distinguished from the original product of Homolle by being easily soluble in water; 120 parts of cold or 40 parts of boiling water. By the action of dilute acid it breaks up into the compounds *digitaliretin*,  $C_{17}H_{24}O_8$ , melting at  $60^\circ$ , and soluble in alcohol and ether, *para-digitaletin*  $C_{22}H_{34}O_{10}$ , melting above  $100^\circ$ , and insoluble in ether, but soluble in alcohol and glucose (cf. Kossmann, J. Ph. [3] 38, 5; Le Fort, J. Ph. [5] 6, 424). Heated with alkalis a compound called *digitalic acid* was obtained by Kossmann. This acid must not be confused with the *digitalic acid* isolated by Morin, together with *antirrhinic acid* from foxglove leaves (J. Ph. [3] 7, 294).

When acetate of lead is added to an aqueous extract of digitalis an insoluble precipitate occurs, which, according to Kossmann, contains two compounds, *digitoleic acid* and *digitaleïn*, which, however, are quite distinct substances from the digitaloic acid of Waltz, or the digitaleïn of Nativelle, to be presently mentioned (J. Chim. Med. [3] 2, 377; Buchn. Rep. 92, 348).

Nativelle, in a series of communications (J. Ph. [4] 15, 192; 9, 255; 16, 430; 20, 81), describes a *crystallised digitalin*. One method

of obtaining this is to exhaust the dried leaves with alcohol, concentrate the solution, and mix with three times its bulk of water, when a precipitate takes place. The precipitate contains the digitalin, together with another compound *digitin*, the former soluble and the latter insoluble in chloroform, and an important amorphous compound *digitaleïn* remains in the solution (v. Palm, Fr. 23, 22). Nativelle's digitalin  $C_{22}H_{34}O_{10}$  (?) consists of rosettes of slender shining needles, which, treated with hydrochloric acid, dissolve with a characteristic emerald-green colour. Flückiger (N. J. P. 29, 129) employs, in the place of hydrochloric acid, warm phosphoric acid, on a watch-glass, to which a few crystals of digitalin are added. The acid becomes yellow and the digitalin of a beautiful green colour (cf. Brunner, B. 6, 86; Fr. 13, 72; Lafon, C. R. 100, 1463; Hock, J. 1881, 977; and Almquist, Ar. Ph. [3] 5, 515). Digitalin is almost insoluble in water and ether, but dissolves in absolute, or, better, in 90 p.c. alcohol, and in chloroform. Digitin  $C_{17}H_{22}O_8$  consists of stellate groups of needles. It is insoluble in water, very slightly soluble in ether, chloroform, and benzene, but soluble in alkalis and hot alcohol. Sulphuric acid dissolves it brown to purple, but it gives no green colour reaction with hydrochloric acid (cf. Goerz, P. Z. 1873, 385 and 417). Of the three constituents discovered by Nativelle digitaleïn is the only one, according to Goerz, possessing marked physiological activity. It is a bitter, light yellow powder. When inhaled through the nose it causes violent sneezing. It is soluble in water and alcohol, and nearly insoluble in ether, chloroform, and benzene. It gives the green colour reaction with hydrochloric acid, and treated with sulphuric acid and bromine changes to red and purple. It contains no nitrogen, and very closely resembles the digitalin of Waltz, which was probably the only important active constituent in the original preparation of Homolle. Like the digitalin of Waltz, digitaleïn yields, when treated with dilute acids, glucose and what appeared to be digitaliretin. Kossmann has studied these compounds further, making numerous analyses (J. Ph. [4] 20, 427); and a new constituent *digitoxin* has been announced by Schmiedeberg (Arch. exp. Path. u. Pharm. 1874, 3, 16). (Cf. Arnaud, C. R. 109, 679, 701.)

Among other compounds contained in foxglove leaves Waltz, by distilling with water, obtained *digitalsmin*, a sort of camphor, and *valerianic acid*.

Foxglove seeds, according to Schmiedeberg, contain a series of compounds, *digitonin*, *digitalin*, and *digitaleïn*, which give rise to several decomposition products. A. S.

#### DIHYDROXY-ACIDS v. HYDROXY-ACIDS.

**DIKA-BREAD.** An edible cake made by the natives of Sierra Leone and the Gaboon from the fruit of the Mango tree, indigenous to most tropical climates. The fruit resembles chocolate in appearance, and contains a large quantity of fatty matter. It has occasionally ripened under hot-house cultivation in this country.

**DIKETONES.** *Dicarbonyl compounds.* The diketones contain two carbonyl groups (CO) attached to hydrocarbon radicles. If the two carbonyl groups are directly united, the compound is an  $\alpha$ -diketone; if they are united by a

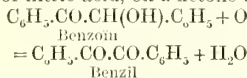


carbon atom, it is a  $\beta$ -diketone; if by a chain of two carbon atoms, a  $\gamma$ -diketone, and so on.

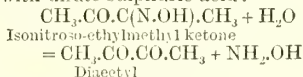
Some of the diketones, such as benzil  $\text{C}_6\text{H}_5\text{CO.CO.C}_6\text{H}_5$ , have been known for a considerable time; but the majority are of recent discovery. Their chief interest lies in the case with which the two carbonyl-groups may be made to condense with one or more molecules of some other substance to form closed-chain compounds. In this way glyoxalines, quinoxalines, pyrazoles, furfurans, pyrroles, thiophenes and similar compounds have been prepared.

Only the more important methods of preparation and reactions of the diketones can be given here.

**$\alpha$ -Diketones.** These may be regarded as homologues of the dialdehyde *glyoxal*  $\text{CHO.CHO}$ . They may be obtained by the action of chlorine, or, better, of nitric acid, on  $\alpha$ -ketone-alcohols:

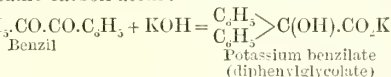


(Laurent, A. Ch. [2] 59, 402; Zimin, A. 34, 183). By hydrolysing the isonitroso-ketones by boiling them with dilute sulphuric acid:

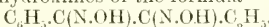


(Von Pechmann, B. 21, 1411).

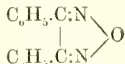
The benzenoid  $\alpha$ -diketones react with *caustic potash* to form secondary glycolic acids, the two hydrocarbon radicals attaching themselves to the same carbon atom:



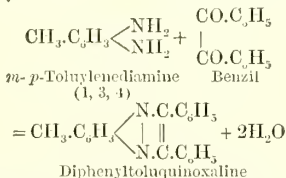
(Liebig, A. 25, 25; Zimin, A. 31, 329). In like manner glyoxal yields glycolic acid. The fatty  $\alpha$ -diketones, however, condense to form quinones (*v. QUINONES*). They react with 2 mols. of *hydroxylamine* to form dihydroximes, which are remarkable for the number of isomeric modifications in which they occur; thus there are three benzil-dihydroximes of the formula



The isomerism is explained by Victor Meyer by means of tridimensional formulæ (Auwers and V. Meyer, B. 22, 705). These hydroximes, when heated, part with water, and form in each case the same closed-chain compound—an anhydride:

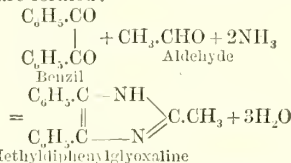


(Auwers and V. Meyer, B. 21, 810). With *o*-diamines the  $\alpha$ -diketones yield quinoxalines (azines):



(Hinsberg, B. 17, 322; cf. Witt, B. 19, 915). With aldehydes and ammonia they react in four different proportions, yielding four distinct

classes of compounds. The most important of these reactions is that in which glyoxaline derivatives are formed:



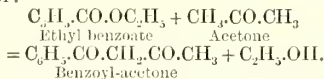
Methylphenylglyoxaline

(cf. Japp and Hooker, C. J. 1884, 672; Japp and Wynne, C. J. 1886, 464).

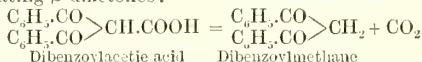
**$\beta$ -Diketones.** The lowest possible member of this series which is a true diketone and not a dialdehyde is acetyl-acetone



By the action of aluminium chloride on acetyl chloride a crystalline substance of the formula  $\text{C}_{12}\text{H}_{10}\text{O}_4\text{Al}_2\text{Cl}_2$  is formed, which, on treatment with water, evolves carbon dioxide and yields acetyl-acetone (Combes, C. R. 103, 814).—A general method for the preparation of  $\beta$ -diketones consists in acting on a mixture of a fatty or a benzene-fatty ketone and the ethyl salt of a carboxylic acid with sodium ethoxide. The latter substance produces condensation between the ethereal salt and the ketone with elimination of alcohol:

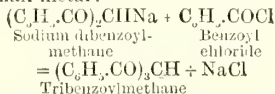


In reality it is the sodium compound of benzoyl-acetone  $\text{C}_6\text{H}_5\text{CO.CHNa.CO.CH}_3$  which is formed, and it is necessary to decompose this compound with carbon dioxide in order to obtain the free diketone (Claisen, B. 20, 655).—Diacidoyl derivatives of acetic acid are decomposed on boiling with water, eliminating carbon dioxide and generating  $\beta$ -diketones:

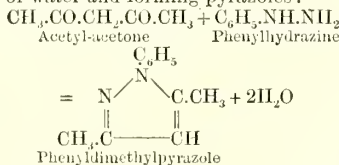


(Baeyer and W. H. Perkin, jun., B. 16, 2128; E. Fischer and Kuzel, B. 16, 2239).

The methylene group in the  $\beta$ -diketones is attached to two electronegative carbonyl groups. For this reason one atom of hydrogen in this group, like the hydrogen in the methylene group of aceto-acetic ether or malonic ether, is replaceable by an alkali metal when the latter is presented to it in the form of an ethoxide. By treating the alkali compound thus obtained with the halogen compound of an alkyl or acid radicle, the radicle can be introduced in place of the alkali metal:



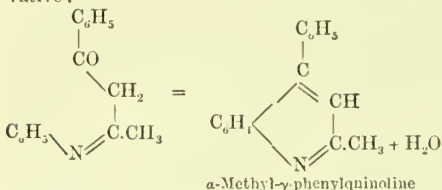
(Baeyer and Perkin, *l.c.*).—The  $\beta$ -diketones react with 1 mol. of *phenylhydrazine*, eliminating 2 mols. of water and forming pyrazoles:



(Knorr, B. 20, 1104).—Aniline reacts with  $\beta$ -diketones in two stages: thus when benzoyl-acetone is heated with aniline to 150° the two substances part with 1 mol. of water:

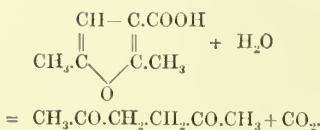


and when the compound thus obtained is heated with concentrated sulphuric acid, it parts with a second mol. of water, forming a quinoline derivative:

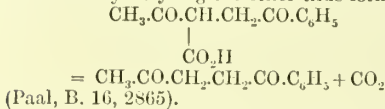


(C. Beyer, B. 20, 1770). This is a general method for the preparation of quinolines containing hydrocarbon radicles in the  $\alpha$ - $\gamma$ -positions.

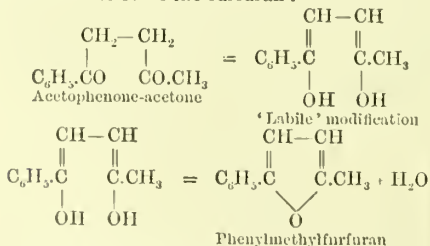
**$\gamma$ -Diketones.** In these compounds the two carbonyl groups are united by an ethylene radicle. The lowest member of the series, acetophenone-acetone, was obtained by Paal (B. 18, 53) by heating pyrotartaric acid with water at 150–160°:



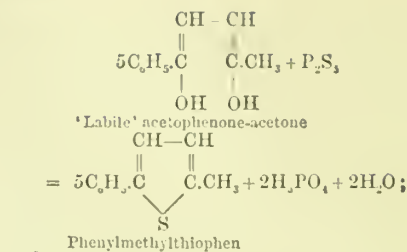
Acetophenone-acetone is obtained by heating acetophenone-acetoacetic acid (prepared by acting with bromacetophenone on sodacetoacetic ether and hydrolysing the ether thus formed):



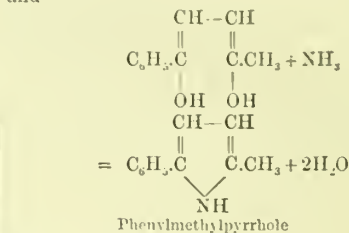
By treatment with *dehydrating agents*, such as fuming hydrochloric acid or acetic anhydride, the  $\gamma$ -diketones are converted into furfurans. It is supposed that in this reaction the diketone first forms a 'labile' modification containing two hydroxyl groups, and that this then parts with water to form the furfuran:



(Paal, B. 17, 2756). An unsaturated ketone isomeric with phenylmethylfurfuran is formed at the same time.—*Phosphorus pentasulphide* converts  $\gamma$ -diketones into thiophenes, whilst with *ammonia* they yield pyrroles, the reaction in both cases being supposed to be preceded by the above-mentioned transformation of the diketone into its 'labile' modification:



and



(Paal, B. 18, 367).

**Quinones.** If the two carbonyl groups of a diketone occur in a closed chain of six carbon atoms, the resulting compound belongs to the class of the quinones. This class of diketones will be treated of separately (*v.* QUINONES).

F. R. J.

**DILATOMETR.** A term originally used to denote a thermometer-shaped apparatus for measuring the thermal expansion of liquids and subsequently given by Silbermann to an instrument for determining the strength of aqueous alcohol.

**DILL OIL** *v.* OILS, ESSENTIAL.

**DIAMYLSAFFRANINES** *v.* AZINES.

**DIMETHYLAMIDONAPHTHAPHENAZINE**

*v.* AZINES.

**DIMETHYLDIAMIDOTOLUPHENAZINE** *v.*

AZINES.

**DIMETHYL ETHYL ACETIC ACID** *v.* FATTY ACIDS.

**DIMETHYLPYRROL** *v.* BONE OIL.

**DIMETHYLAMINE ORANGE** *v.* AZO-COLOURING MATTERS.

**DIMETHYL ORANGE** *v.* AZO-COLOURING MATTER.

**DIMETHYLSAFFRANINES** *v.* AZINES.

**DINICOTINIC ACID** *v.* BONE OIL.

**DINITROSORESORCIN** *v.* RESORCIN.

**DIOSCOREA.** A genus of plants of the Smilacaceae order, the tubers of which are known as yams, and are largely eaten in the West Indies and other tropical countries.

**DIOSPHENOL** *v.* CAMPHORS.

**DIOXYBENZOIC ACID** *v.* HYDROXY-ACIDS.

**DIPHENAZINE** *v.* AZINES.

**DIPHENIC ACID** *v.* PHENANTHRENE.

**DIPHENYL**  $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5$  is formed when phenyl is liberated from its combinations, two phenyl groups uniting to yield diphenyl. First obtained by Fittig (A. 121, 363) by the action of sodium on an ethereal solution of bromobenzene. Best prepared by Berthelot's method of passing the vapour of benzene through a red-hot tube

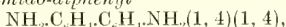
$2\text{C}_6\text{H}_6 = \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5 + \text{H}_2$   
(A. Ch. [4] 9, 453; [4] 12, 185). Schultz, who has examined the various methods for preparing

diphenyl, adopts that of Berthelot and recommends the following procedure (A. 174, 202; *Chemie des Steinkohlentheers*, 1, 193). An iron tube is heated to redness in a Hofmann's gas furnace, which is raised at one end so as to cause the tube to slope downwards. The upper end of the tube is connected by a cork and bent adapter with a dropping funnel through which the benzene is delivered at the rate of 3 drops per second; the lower end leads to a receiver in which the products are condensed. On redistillation these yield, first benzene, then diphenyl, and lastly diphenyl-benzene and other hydrocarbons of high boiling-point. The portion boiling between 250 and 300° consists of almost pure diphenyl; this is redistilled and the fraction passing over between 250 and 260° is purified by recrystallisation from alcohol. If commercial benzene containing thiophen has been employed, the product contains *dithienyl* ( $C_8H_6S_2$ ) (m.p. 83°), which gives a magnificent blue colouration with isatin and sulphuric acid.

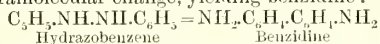
Crystallises from alcohol in large lustrous laminae melting at 70·5°. Boils at 254° (cor.). Insoluble in water; readily soluble in hot, sparingly soluble in cold alcohol. When heated with a solution of chromic anhydride in acetic acid it is oxidised to benzoic acid.

Diphenyl yields with the halogens, with nitric acid and with sulphuric acid, substitution derivatives which correspond with those obtained from benzene. The substitution may be effected either only in one nucleus or in both, according to the conditions of the reaction.

**Benzidine.** This important base, which is *dipara-amido-diphenyl*



is formed by the reduction of the corresponding dinitrodiphenyl (m.p. 233°) with tin and hydrochloric acid (Fittig, A. 124, 276). It is most readily prepared, however, from hydrazobenzene, which in contact with acids undergoes a peculiar intramolecular change, yielding benzidine:



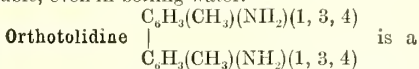
(Zinin, J. pr. 36, 93; Hofmann, Pr. 12, 576).

In order to prepare it, 10 parts of azobenzene  $C_6H_5 \cdot N : N \cdot C_6H_5$  are dissolved in alcohol and warmed for some time with a solution of  $3\frac{1}{2}$  parts of tin in concentrated hydrochloric acid. The stannous chloride reduces the azobenzene to hydrazobenzene, which is at once transformed by the acid into benzidine hydrochloride. A certain quantity of diphenyl-ine (ortho-paradiamidodiphenyl, isomeric with benzidine) is also formed during the transformation, and a part of the azobenzene is reduced to aniline. In order to separate the benzidine, the alcohol is distilled off, the residue dissolved in water, and sulphuric acid added to the solution. This precipitates sparingly soluble benzidine sulphate, whilst the sulphates of diphenyl-ine and aniline remain in solution. The benzidine sulphate is separated by filtration, washed with dilute hydrochloric acid (to remove tin compounds), decomposed with ammonia and the benzidine purified by recrystallisation from dilute alcohol.

On a large scale, benzidine is prepared by heating nitrobenzene with caustic soda and the calculated quantity of zinc-dust necessary to

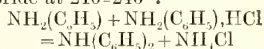
reduce the nitrobenzene to hydrazobenzene, adding a little alcohol; washing the hydrazobenzene with cold dilute hydrochloric acid to remove zinc hydroxide, and converting it into benzidine by dissolving it in hot dilute hydrochloric acid.

Large lustrous laminae, colourless when pure, but generally reddish-coloured from oxidation. Melts at 122° and boils with partial decomposition above 360°. Very sparingly soluble in cold, more soluble in boiling water. Chlorine water, or a solution of bleaching powder, converts it into a reddish substance. With nitrous acid benzidine salts form tetrazo- (di-diazo-) salts, which on boiling with alcohol yield diphenyl. These tetrazo- salts react with phenols, phenol-sulphonic acids, amido-sulphonic acids, and similar compounds to form azo- colours (*Congo red*, *Chrysamin* v. AZO-COLOURING MATTERS) which are remarkable for the property of dyeing cotton without a mordant. Benzidine forms crystallised salts; the sulphate is very sparingly soluble, even in boiling water.



derivative of *meta-ditolyl* and is prepared from orthonitrotoluene by the same process by which benzidine is obtained from nitrobenzene. It forms lustrous laminae melting at 128°, and resembles benzidine in its properties and reactions. The azo- dyes obtained from it correspond with those from benzidine, and like these dye unmordanted cotton, but have the advantage of being less easily altered by acids. F. R. J.

**DIPHENYLAMINE**  $NH(C_6H_5)_2$ . First obtained by Hofmann, in 1864, by the distillation of aniline blue (triphenylrosaniline) (A. 132, 163), and in small quantity by the distillation of rosaniline and leucaniline. De Laire, Girard, and Chapoteaut showed that it could be more readily prepared by heating aniline with aniline hydrochloride at 210–240°:



(C. R. 63, 91). By heating phenol with the double compound of aniline and zinc chloride at 250–260°:



(Merz and Weith, B. 13, 1298).

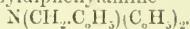
**Manufacture.**—Aniline (1 mol.) is heated with aniline hydrochloride ( $\frac{1}{2}$  mol.) for from 30 to 35 hours in an autoclave at 220–230°. The product of the reaction is treated, while still warm, with strong hydrochloric acid, and then with an excess of water, which dissolves the aniline salt, but decomposes the diphenylamine salt into free acid and base, the latter separating as an oil, which speedily solidifies. The cake of diphenylamine is washed, and then distilled, either alone or in a current of steam. The yield is from 60 to 70 p.c.

**Properties.**—Monoclinic laminae, melting at 54°. Boils at 310°. Almost insoluble in water; soluble in alcohol, benzene, and ether. Feebly basic; the salts are decomposed by excess of water.

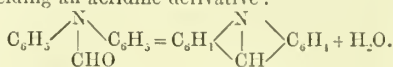
**Reactions.**—The hydrogen of the imido-group in diphenylamine may be replaced by alkyl groups or by acid radicles. Thus, when heated with methyl iodide it yields methyl-



diphenylamine  $N(CH_3)(C_6H_5)_2$ , and with benzyl chloride, benzyl-diphenylamine



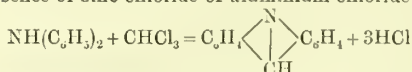
By heating it with acids of the acetic series or their chlorides, the acid radicles may be introduced: thus with acetic acid acetyl-diphenylamine is formed. If zinc chloride is added in the foregoing reaction the acidoyl-diphenylamine first formed parts with a mol. of water, yielding an acridine derivative:



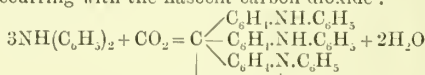
Formyl-diphenylamine

Acridine

In like manner acetyl-diphenylamine yields methylacridine (Berntsen and Bender, B. 16, 767). Diphenylamine is also converted into acridine by heating it with chloroform in presence of zinc chloride or aluminium chloride:

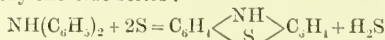


(O. Fischer and Körner, B. 17, 101). When heated with excess of oxalic acid, diphenylamine yields diphenylamine blue, condensation occurring with the nascent carbon dioxide:

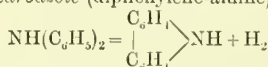


Diphenylamine blue (anhydrous triphenyl-pararosaniline).

Carbon tetrachloride acts like the nascent carbon dioxide in the foregoing reaction, forming diphenylamine blue. When heated with sulphur, diphenylamine yields thiodiphenylamine, the parent substance of the colouring matters of the methylene-blue series:



(Berntsen, B. 16, 2897). When the vapour of diphenylamine is passed through a red-hot tube it forms *carbazole* (diphenylene-amine):



(Graebe, A. 167, 127). When nitrated in acetic acid solution it yields tetranitro-diphenylamine; but by direct nitration hexanitro-diphenylamine is formed, which acts as an acid, and in the form of its ammonium salt is used as a yellow dye under the name of *aurantia*. Amyl nitrite converts diphenylamine into nitroso-diphenylamine  $N(NO)(C_6H_5)_2$ . With bromine it yields bromo-derivatives, and with concentrated sulphuric acid sulphonic acids. A solution of diphenylamine in concentrated sulphuric acid is coloured blue by a trace of nitric or nitrous acid; and diphenylamine is therefore used as a test for the presence of oxides of nitrogen in sulphuric acid (Kopp, B. 5, 284). Chloric acid produces the same colouration. Oxidised with potassium permanganate diphenylamine yields diphenyl-azophenylene  $C_{18}H_{11}N_2$  (Bandrowski, M. 7, 375).

Diphenylamine is employed in the manufacture of diphenylamine blue, diphenylamine orange, and *aurantia*. The commercial product should be a pale yellow solid, uncontaminated by oily matters, and should melt not much below  $51^\circ$ . It should not have any unpleasant odour,

should not turn rapidly brown on exposure to air, and should give no aniline reaction with bleaching powder.

**Tertiary bases derived from diphenylamine.**

**Methyldiphenylamine**  $N(CH_3)(C_6H_5)_2$ . By warming diphenylamine with methyl iodide on the water-bath. By heating diphenylamine hydrochloride under pressure with methyl alcohol, at  $250-300^\circ$  (Bardy, Eng. Pat. 376, 1870; B. 3, 838; Girard and Vogt, J. pr. [2] 4, 289). The hydrochloride dissociates at the temperature of the reaction, and the liberated hydrochloric acid reacts with the methyl alcohol, forming methyl chloride, which in its turn acts on the diphenylamine, converting it into methyldiphenylamine. The latter base can be separated from unaltered diphenylamine by converting both into hydrochlorides; methyldiphenylamine forms a liquid hydrochloride, whilst that of diphenylamine is solid.

Methyldiphenylamine is an oil, boiling at  $282^\circ$ . Its salts are decomposed by water. Arsenic acid and the other oxidising agents used in the preparation of rosaniline convert it into blue colouring matters. When heated with oxalic acid it yields methyldiphenylamine blue, the sulphonic acids of which are employed as dye-stuffs.

**Ethyldiphenylamine**  $N(C_2H_5)(C_6H_5)_2$ . Prepared like the foregoing. Liquid boiling at  $295-297^\circ$ . When heated with oxalic acid it yields a blue colouring matter.

**Amyldiphenylamine**  $N(C_3H_7)(C_6H_5)_2$ . Boils at  $330-340^\circ$ , and gives a blue colouring matter on heating with oxalic acid.

**Benzyl-diphenylamine**  $N(C_6H_5)(C_6H_5)_2$ . Obtained by the action of benzyl chloride on diphenylamine. Deposited from its solution in alcohol, ether, or benzene in crystals, melting at  $87^\circ$ . By treatment with arsenic acid and hydrochloric acid, chloranil, and other oxidising agents, the substance thus prepared yields bluish-green compounds, the alkali sulphonates of which have been used as green colouring matters under the names of *viridine* and *alkali green*; but Meldola has shown (C. J. 1882, 187) that these colouring matters belong to the malachite green series and are produced by the oxidation of a leuco-compound, the formation of which is due to benzal chloride  $C_6H_5 \cdot CHCl_2$ , contained in the commercial benzyl chloride.

F. R. J.

**DIPHENYLAMINE BLUE v. TRIPHENYL-METHANE COLOURING MATTERS.**

**DIPHENYLAMINE YELLOW v. AZO-COLOURING MATTERS.**

**DIPHENYLENE-METHANE v. FLUORENE.**

**DIPHENYLTOLUAZINE v. AZINES.**

**DIPICOLINIC ACID v. BONE OIL.**

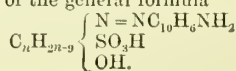
**DIPPEL'S OIL v. BONE OIL.**

**DIPROPYLACETIC ACID v. FATTY ACIDS.**

**DIPYRIDINE v. BONE OIL.**

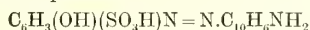
**DIPYRIDYL v. BONE OIL.**

**DISAZO and TETRAZO-COLOURING MATTERS.** The sulphonic compounds of amido-phenols combine with  $\alpha$ -naphthylamine, and form compounds of the general formula



These bodies, being again diazotised and coupled with  $\alpha$ - and  $\beta$ -naphtholsulphonic acids, produce colouring matters showing great fastness to light on the fibre.

To prepare these bodies, 21.5 kilos. of sodium amido-*p*-phenol sulphonate are diazotised with 7 kilos. of sodium nitrite, hydrochloric acid being added to the mixture of these two compounds. Then 20 kilos. of naphthylamine hydrochloride are added, and after a short time the new compound



separates from the solution. At ordinary temperatures the combination is finished in several days, but it can be accelerated by warming from  $40^\circ$ – $50^\circ\text{C}$ . As soon as a sample, after filtration and standing, does not produce any more colouring matter, the dark-green precipitate is filtered

and washed. It dissolves in sulphuric acid with a dark-violet colour, in ammonia with a brown-orange colour. The precipitate is dissolved in 10 kilos. of ammonia of 17 p.c., and to this solution 7 kilos. of ammonia are added. The mixture is poured into hydrochloric acid, which is cooled with ice. The diazo-compound thus formed has a pure brown colour, and is treated with 38 kilos. of R. salt. The colouring matter obtained forms a black precipitate. It dissolves in sulphuric acid with a blue colour, and dyes wool violet to violet black. Similar dyestuffs are obtained from amidophenol sulphonic acid,  $\alpha$ -naphthylamine, and Schäffer's  $\beta$ - and  $\alpha$ - (Neville and Winter's), naphthol-sulphonic acid, and from amido-ortho-cresol-, and amido-para-cresol-sulphonic acid. The following table shows the reactions of the cresol derivatives:

Properties	Colouring matters from					
	Amido-ortho-cresol-sulphonic acids with			Amido-para-cresol-sulphonic acids with		
	Schäffer's $\beta$ -naphthol monosulphonic acid	R. salt	Neville and Winter's $\alpha$ -naphthol monosulphonic acid	Schäffer's $\beta$ -naphthol monosulphonic acid	R. salt	Neville and Winter's $\alpha$ -naphthol monosulphonic acid
Colour of powder	Greenish-black of a metallic lustre.	Brownish-violet of a metallic lustre.	Brownish-black of a metallic lustre.	Greenish-black of a metallic lustre.	Dark brown of a bronze appearance.	Dark green of a metallic lustre.
Colour of solution in ammonia.	Red-violet . Blue-violet .	Blue-violet . Blue . . .	Blue-violet . Red-violet .	Blue-violet . Blue . . .	Blue-violet . Blue . . .	Violet. Blue.
Colour of solution in hydrochloric acid.	Red-violet .	Blue-violet .	Red-violet .	Dark - violet precipitate .	Violet precipitate .	Violet.
Action of concentrated sulphuric acid.	Dark green .	Dark green	Dark green .	Dark green .	Dark green .	Dark green.

Zeits. f. Angew. Chem. 1889, 50–52, and S. C. I. 8, 279.

**DISCRASITE.** *Silver antimonide* v. ANTIMONY.

**DISINFECTANTS.** A disinfectant in a general sense is a body which will destroy the disease-germs which abound in an impure atmosphere and infest the very substance of a body undergoing decomposition.

The true meaning of the term disinfectant appears to have been much misunderstood, and indeed confusion still exists respecting it. It is perhaps most correct to regard as disinfectants such bodies as will kill, by one of many different means, germs or other living organisms (be they of animal or vegetable nature) which are capable, by contagion or otherwise, of acting injuriously on the higher forms of life.

It will be seen from this that the term disinfectant implies much more than a mere *preservative* which acts by *preventing* putrefaction. For example, the addition of alcohol to almost any vegetable or animal substance, in a sound condition, will prevent such substance from undergoing decomposition; but at the same time alcohol can only be considered as a disinfectant in the light that it will prevent putrefaction.

On the other hand, a very small quantity of chlorine or bromine will do more than merely preserve the substance, for should any germs be already present, they will be killed if placed in

an atmosphere containing either element, and if the substance which it is desired to disinfect be kept constantly in contact with free chlorine or bromine, new germs cannot possibly, under such conditions, be formed.

Those agents which prevent putrefaction, but which have not the power of destroying actual germ life, are termed *Antiseptics*. In the instance above alluded to, alcohol would act as an antiseptic. Thus, while an antiseptic agent is not necessarily a disinfectant, all disinfectants are antiseptics.

A third class of substances known as '*Deodorisers*' form a still less active group. These bodies have the power of absorbing unpleasant odours arising from the decay of organic matter, but do not act as disinfectants or antiseptics.

Animal matter undergoing eremacausis evolves gases having a most fœtid odour, but if these gases be made to pass through a somewhat compact bed of recently burnt charcoal, the objectionable odour is removed. In this case, so far as the present state of our knowledge extends, it would appear that charcoal does not remove or kill the bacteria themselves, but that it absorbs the offensive gases and destroys them by oxidation in the pores or in other manner. Charcoal can be made to act as an antiseptic only to a very limited extent, if at all, even when brought into immediate contact with the sub-

stance to be preserved, but it always acts as a deodoriser if the porosity be maintained and it is duly aerated.

One of the first applications of disinfectants was probably that involved in the ancient process of embalming the dead by treatment with aromatic gums, resins, &c. Other methods of preserving the dead were in use by the ancients, such as asphaltung and salting the entire body. Desiccation was also used as a means of preventing the decay of bodies, and the condition of some of the Egyptian mummies seems to confirm the belief that this played an important part also in the embalming processes of Egypt. Desiccation, when properly applied, is one of the surest methods of preventing flesh from undergoing *eremacausis*, and forms the subject of a modern patent. Almost any organic substance which is kept thoroughly desiccated will remain unaltered for an indefinite period. Yeast, for example, which is most prone to decompose under ordinary conditions, will keep for a long time if thoroughly and carefully desiccated, and, provided the temperature does not exceed a certain limit, the vitality of the yeast will not be affected by such treatment.

The soil is a very powerful deodoriser, and acts to some extent as an antiseptic. Most of the gases resulting from the burial of the dead are completely absorbed and rendered innocuous by the immediately surrounding soil.

For a long time it was thought that putrefaction took place spontaneously without any definite cause, but we now know that such is not the case. It has been proved, beyond doubt, that *eremacausis* is due to the presence and activity of living germs. These living germs pervade the atmosphere, even where it is purest, and exist to a very large extent in districts where life is abundant.

Infectious diseases are conveyed by direct or indirect contact with infected persons or things, and the 'disease-germs,' as they are called, carry with them the power of infection.

It was thought for many centuries that maggots, such as occur in decomposed flesh and similar substances, were the result of spontaneous generation. This was disproved in 1668 by Francesco Redi, who placed some wire gauze over a jar containing meat. The flies which were attracted, being unable to get at the meat, deposited their eggs on the metallic gauze, and in due time these produced maggots.

It has been found that a still, warm, and moist atmosphere induces the spread of infection. The atmosphere is the great carrier for the products of the decomposition of organic matter. Hence, when matter which is undergoing decomposition is exposed to the air, the removal may be attended with considerable risk, unless it is properly treated. Tyndall has proved that the air is largely laden with dust in the finest state of division, and associated with this dust are germs capable of causing organic matter to be decomposed. These dust particles and germs can be removed by the simple expedient of passing the air through somewhat compact cotton wool. This forms a perfect filtering medium for such a purpose.

According to M. Pasteur, on exposing a putrescible liquid to the air, there forms on the

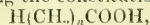
surface a film of *bacteria*, which exclude completely any oxygen from the liquid by themselves rapidly absorbing that gas. Beneath these bacteria other more active organisms, which Pasteur groups together under the name of *vibrios*, act as ferments upon the albuminous matters of the liquid, and decompose them into simpler products.

These in their turn are oxidised still further by the surface bacteria. Pasteur practically defines *putrefaction*, or putrid fermentation, as fermentation without oxygen. This most important fermentation of albuminous matter, viz. putrefaction, is occasioned by *Bacterium termo* (0.0015 to 0.002 mm. long), and it is this bacterium which induces the decay of all organic matter, and appears to preserve the equilibrium between animal and vegetable life.

In consequence of the imperfection of our knowledge of the structure of the proteid compounds, that is, of the material which affords septic bacteria their soil, the chemical investigation of the process is one of extreme difficulty. Some light is thrown on its nature by the knowledge we possess of decompositions evidently analogous to it, to which bodies of known constitution are liable under corresponding conditions. Among the best examples of these, the decomposition of calcium formate and acetate under the influence of septic ferment may be referred to (the former yielding  $\text{CO}_2$  and  $\text{H}_2$ , the latter  $\text{CO}_2$  and  $\text{CH}_4$ ), and the decomposition of lactic acid (yielding butyric acid and hydrogen), the most remarkable feature in these processes being the prevalence of strong reducing agents in the liquids undergoing decomposition.

In general the putrefaction of proteid matter begins by the transformation of the proteid material itself, first into *albuminates*, i.e. bodies soluble in liquids of acid or alkaline reaction, but precipitated on neutralisation; secondly, into *peptones*, by which term is meant a proteid body which is soluble in all aqueous liquids, acid, alkaline or neutral, and at all temperatures. The second stage in putrefaction consists in the breaking up of these soluble proteids, so as to give rise to compounds more simple and definite in composition, of which the most important are the well-known substances, leucine, tyrosine, and indol. Indol and tyrosine with their derivatives belong to the aromatic group, the members of which are linked together, not only by their chemical structure and relations, but also by that physiological property which, so far as we know, is possessed by all of them in greater or less degree, namely, antagonism to the life of ferment organisms (microzymes).

Inasmuch as in the septic process the initial material is proteid and the end-products are ammonia and carbon dioxide, there is an obvious resemblance between it and that of the exchange of material in the animal body, the difference being in the intermediate stages; but even here the analogy holds good in certain important respects. It is alike characteristic of both that organic acids belonging to the acetic series, i.e. having the constitution:—



are produced in such quantity as to represent a large proportion of the initial material. In the metabolism of the higher animals these occur



as glycerides of the higher fatty acids; in the bacterial process in the form of the alkali-metal or ammonium salts of lower acids of the same series. The analogy which has just been referred to derives its importance from the consideration that in the production of all infective diseases, from inflammation to the specific infections, the two processes are concomitant and at the same time antagonistic. Whatever hope we may entertain of eventually acquiring a complete understanding of the nature of this antagonism must be founded on the knowledge which we now possess or may in future possess of the relations between the two processes, *i.e.* of the influences which they mutually exercise on each other in the living organism of man and the higher animals.

From this general statement it is obvious that bacterial life, regarded from a chemical point of view, that is to say, with reference to the question of the initial material (protein) and the end-products ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ ), corresponds closely with that of animal life in general. For while bacteria feed on protein matter and convert its material into the simple compounds above enumerated, the higher animal organisms in their processes of digestion and assimilation arrive eventually at the same result. The difference lies chiefly in the intermediate stages; in both, bodies belonging to the acetic acid series are produced in such quantity as to represent a large proportion of the initial material; in the first the bodies include the lower members of the fatty acid groups, whilst in the second the higher members appear as glycerides or fats.

The mode in which the presence of septic organisms in the living body of man and animals can be best understood is by recognising the essential correspondence which exists between their vital processes. It is because the vital processes of the bacterium so closely resemble those of the animal with which it associates itself that the one comes into such relation with the other as to exercise a modifying (that is to say, a disease-producing) influence upon it. Whatever the nature of its influence may be, it is obviously chemical.

Four distinct classes of aromatic compounds occur as products and concomitants of bacterial life, namely:—

1. *Phenols*, the presence of which in urine was first observed by Salkowski, and the occurrence of which is apparently associated with that of *indican*. 2. *Indol*. 3. *Tyrosine* and septic derivatives of that body. 4. *Acids of the benzoic series*, especially phenylpropionic acid.

Dr. Hamilton has expressed the view (British Medical Association, Dublin Meeting, August, 1887) that attention hitherto has been too exclusively fixed upon the germs, and sufficient regard has not been had to the influence of environment. Every effort has been strained simply to discover the most deadly germicide, although it is known that the germs, however virulent they may be, cannot undergo their life-changes and produce their effective results unless their environment, like the cultivation-fluid of the histo-pathologists, is capable of developing and sustaining these changes. Deposited on clean metal, glass, or porcelain, the organisms

die of inanition; they exercise no influence whatever, and are amenable to none. But in contact with dead organic matter, or living matter in certain conditions of altered or reduced vitality, they become a teeming source of decomposition and decay. If, therefore, pathological surfaces could be brought to and maintained in such a condition that they would not afford a suitable cultivation-ground, almost as much would be accomplished as if the germs were actually destroyed. This point Dr. Hamilton illustrates in various ways, and testifies to the good results obtained in treating open wounds with a solution of chloride of zinc.

The experiments of Le Bon bear out Hamilton's view, and show clearly that not only the antiseptic but also the condition of the substance to which it is applied exercises a powerful influence upon its action, and hence ought to be taken into account. As an example, an aqueous liquid containing 10 p.c. of minced flesh gives off at the commencement of putrefaction an odour which is very fetid, but which is destroyed by a relatively small amount of an antiseptic. If instead of this, however, the putrefaction be allowed to continue for some time, say two months, new bodies will be developed, having distinctly different odours and requiring at least twice the amount of antiseptic for their destruction.

Working upon a liquid prepared from minced flesh, Le Bon has proved that the order of position which various antiseptics take is very different from that commonly supposed. Thus we find in order of merit:—potassium permanganate, chlorinated lime, ferrous sulphate acidified with acetic acid, carbolic acid, glyceroborates of sodium and potassium. Le Bon concludes that there appears to be no relation existing between the power of preventing the *initiation* of putrefaction and that of *arresting* putrefaction when it has commenced; that most of the reputed antiseptics have little power upon bacteria; and that mercuric chloride is one of the most powerful germicides. Le Bon is of opinion that no parallelism exists between the virulent nature of a putrefying body and the toxic power of the volatile compounds that are given off from it. He states that the extremely toxic nature of the volatile products of putrefaction was on more than one occasion demonstrated upon himself and other persons who happened to enter his laboratory during the course of his experiments.

Germs evidently possess different powers of vitality, *i.e.* some germs are better able to combat with a particular disinfectant than others, so that it is impossible to judge from one kind of germ the effect upon another. Thus experiments by Arloing, Cornevin, and Thomas, on the influence of various disinfectants upon the virus of symptomatic anthrax, showed that the following antiseptics had no action on the fresh virus:—solution of camphor or phenol in alcohol, glycerin, ammonia, acetate and sulphate of ammonium, benzene, saturated solution of sodium chloride, quicklime and lime-water, polysulphide of calcium, 50 p.c. solution of sodium thiosulphate, 20 p.c. solution of borax, tannic acid, manganous chloride and ferrous sulphate, 10 p.c. solution of quinine sulphate, turpentine, and

monobromide of camphor; of gases, ammonia, sulphurous anhydride and chloroform vapour.

The following substances had an action sufficient to kill the fresh virus, but did not kill that which had been dried:—Saturated solution of oxalic acid, 5 p.e. solution of potassium permanganate, 20 p.e. solution of sodium hydrate, chlorine, and vapours of carbon disulphide. The following killed the virus which had been dried:—20 p.e. aqueous solution of phenol, 0.1 p.e. solution of salicylic acid, 0.1 p.e. solution of silver nitrate, 20 p.e. solution of copper sulphate, 20 p.e. solution of boric acid, saturated alcoholic solution of salicylic acid, 0.02 p.e. solution of mercuric chloride, and bromine vapour. It will thus be seen that many substances which are, and have been, for a long time credited with antiseptic powers, are in reality of no use as such so far as this disease is concerned. It is still customary, for example, to bury in quicklime animals which have died from anthrax. It may be that the only effect which lime has upon organisms of such a nature lies in the heat evolved at the moment of hydration. A striking instance of the different powers of resistance possessed by different bacteria is found in the fact that sulphurous anhydride, which usually is one of the most successful germi-

cides, has no effect upon the fresh virus of anthrax. Bromine vapour seems to be the only vapour which can satisfactorily destroy the virus. Mercuric chloride stands first on the list of germicides for this particular disease, a solution of 1 in 5,000 being sufficiently active to destroy the virus. Silver nitrate, salicylic acid and carbolic acid follow mercuric chloride in importance. It was found, however, by Arloing, Cornevin, and Thomas that to be effective a 2 p.e. solution of carbolic acid had to remain in contact for 8 hours in the case of the fresh virus, and for 24 hours in the case of the dried virus.

Ratimoff has experimented upon the relative activity of antiseptics on septic and putrefactive bacteria and also on microbes. Determinations were made of the quantity of each antiseptic required to kill or to sterilise. From the results of these investigations the antiseptics are arranged in the following order of activity: Mercuric chloride, silver nitrate, iodine, thymol, copper sulphate, salicylic acid, zinc chloride, phenol, quinol, kairine, resorcinol, chloral hydrate, boric acid, alcohol, oil of wintergreen, bitter almond oil, eucalyptus oil. The following table illustrates the mode of observation and the action on meat-broth of some antiseptics, diluted as indicated:—

Antiseptic	Microbes		Bacteria			
			Putrefactive		Septic	
			Killed	Not killed	Killed	Not killed
Mercuric chloride . . .	1 : 13,300	1 : 25,000	1 : 800,000	1 : 1,000,000	1 : 66,700	1 : 100,000
Thymol . . . . .	1 : 2,000	1 : 5,000	1 : 35,000	1 : 50,000	—	—
Salicylic acid . . . .	1 : 400	1 : 500	1 : 1,200	1 : 2,000	1 : 1,000	1 : 2,000
Phenol . . . . .	1 : 400	1 : 500	1 : 570	1 : 670	—	—

The following is a tabulation of experiments made by Dr. Crace Calvert upon albumen solution.

In each case the number of days was noted before vibrio life appeared in a solution of albumen containing 1 of substance in 1,000 of solution:—

Substance used	Animalcules	Putrid odour	Fungi	Mouldy odour
<i>Acids:</i>				
Sulphurous . . . .	11	over 40	21	over 40
Nitric . . . . .	10	50	10	23
Sulphuric . . . .	9	—	9	11
Carbolic . . . . .	over 40	over 40	over 40	over 40
Cresylic . . . . .	"	"	"	"
Acetic . . . . .	30	"	"	50
Phoric . . . . .	17	over 40	19	over 40
<i>Alkalis:</i>				
Lime . . . . .	13	19	over 40	over 40
Potash . . . . .	16	—	—	—
Soda . . . . .	23	31	18	29
Ammonia . . . . .	24	50	20	over 40
Chlorine gas . . .	7	21	21	—
Chlorinated lime .	7	18	16	—
Chloride zinc . . .	over 40	over 40	50	over 40
Chloride aluminium	10	21	21	50
Bisulphite calcium	11	21	11	over 40
Sulphate iron . . .	7	over 40	15	—
Potassiumate potash	9	50	22	over 40
Turpentine oil . . .	14	over 40	42	"

In the above experiments by Dr. Crace Calvert, 0.026 of a gramme of the substance

was added to 26 grammes (1 to 1,000) of a solution of albumin containing 1 part white of egg to 4 parts pure distilled water.

Putrefaction was always characterised by a putrid odour, an alkaline reaction, and the presence of animalcules; whereas mouldiness and fermentation were distinguished by a mouldy or musty odour, an acid reaction, and the presence of fungi.

The following table summarises a number of experiments made by Dr. John Dougall and Dr. Crace Calvert on the action of various antiseptics on protoplasmic and fungus life.

The animalcules observed were Monads (microphytes), Vibrios, and their cell-segments (microcoryphes), Bacteria (microzymes), Amoebæ, &c.; and the fungi were Torula, Mycelium, Penicillium, &c., indicated in the table by letters T. and P.

In the first set of these experiments by Dr. J. Dougall, 6 volumes of a solution of the strength mentioned were treated with 2 volumes of a filtered infusion of hay, or with urine, or a mixture of beef juice and egg albumen. In the second set of experiments equal parts of a putrid solution of beef juice and egg albumen, full of living animalcules and of the solution of various substances of the strength known to be preventive of life (as in fifth column), were mixed together, and the results immediately

Substances used	Reaction of the solution	Quantity required to prevent animalcules in six days				Effect on animalcules in putrid beef juice and egg albumen when added in proportion in fifth column	Number of days before life appeared in a solution containing 1 of substance in 500 water and $\frac{1}{2}$ drachm of following :				Effect of the vapour or gas during 24 hours on vaccine lymph	
		Beef juice and egg albumen					Beef juice		Solution of egg albumen			
		Infusion of hay	Human urine	Beef juice and egg albumen	Average of all		Animalcules	Fungi	Animalcules	Fungi		
<i>Acids—</i>												
<i>Inorganic :</i>												
Sulphurous . . .	Acid	1 in 250	1 in 50	1 in 50	1 in 117	Death	24	4 P.	8	over 100	Killed	
Nitric . . .	"	400	400	200	333	"	18	4 P.	15	5 T.	"	
Hydrochloric . . .	"	500	400	100	333	"	28	4 P.	9	over 100	"	
Sulphuric . . .	"	800	500	100	467	"	over 100	over 100	30	10 T.	"	
Chromic . . .	"	4,000	1,400	1,200	2,200	—	78	38 P.	over 100	over 100	—	
<i>Organic :</i>												
Carbolic . . .	Neutral	300	300	200	267	None	12	50 T.	38	36 P.	None Killed	
Acetic . . .	Acid	350	25	10	125	—	—	—	—	—	—	
Picric . . .	"	350	350	350	350	Death	44	11 P.	over 100	44 P.	—	
Benzoic . . .	"	700	700	200	533	"	over 100	over 100	"	over 100	—	
Potash . . .	Alkaline	300	50	10	120	Death	—	—	—	—	—	
<i>Haloids :</i>												
Iodine tincture . . .	Neutral	400	400	50	283	Death	1	80 T.	15	over 100	—	
Chlorine gas . . .	Acid	—	—	—	—	—	27	27 T.	40	over 100	Killed	
Chloride of lime . . .	Alkaline	200	200	25	142	Death	4	over 100	18	"	"	
" " zinc . . .	Acid	300	300	300	300	"	19	4 P.	over 100	8 P.	—	
" " aluminium . . .		2,000	500	300	933	—	—	—	—	—	—	
<i>Sulphates, &amp;c. :</i>												
Calcium bisulphite . . .	Acid	100	50	25	58	Death	4	92 T.	9	over 100	—	
Zinc sulphate . . .	"	300	300	200	267	"	30	4 P.	90	70 P.	—	
Iron . . .	"	500	500	100	367	?	14	5 T.	35	40 T.	—	
Common alum . . .	"	800	500	100	467	—	14	3 P.	38	15 T.	—	
Copper sulphate . . .	"	1,000	1,000	800	933	Death	86	20 P.	over 100	over 100	—	
Potassium permanganate . . .	Neutral	500	200	125	275	None	—	—	—	—	—	
Alcohol . . .	"	350	50	20	140	Death	4	4 T.	10	over 100	—	
Camphor . . .	"	300	150	50	167	None	—	—	—	—	None	



noted. In the third set of experiments  $3\frac{1}{2}$  drachms of distilled water, containing 1 in 500 of the substances named, were treated with half a drachm of filtered beef juice, or half a drachm of a solution consisting of 1 part white of egg to 4 parts water. In the last set of experiments separate minims of vaccine lymph were exposed to the several vapours for 24 hours, and the dried spot in each case was moistened with glycerine and water and sealed in a capillary tube until an opportunity for vaccination occurred, when the whole of the diluted lymph was used in one insertion so as to ensure its full effect.

In the opinion of R. Koch (Chem. Centr. 1882, 509) an efficient disinfectant ought to kill all living organisms and render all germs innocuous within twenty-four hours. To test a disinfectant thoroughly, its action must be tried on all disease-producing matter, and under conditions exactly similar to those in which it is used in practice. Thus a disinfectant which does not kill fungi would be of no use in contagious skin diseases; whilst one which does not destroy bacteria would be inefficient in diseases caused by these organisms.

Koch has investigated the action of disinfectants on bacteria. In these experiments great care was taken in the cultivation of bacteria, selecting those which are seldom found in the air. The experiments on the development of bacteria were made on solid nutritious substances. The chief points observed were—1. If all the organisms were killed, for which purpose it was sufficient to note the action on the most persistent—viz. the bacilli spores; 2. The facility with which the development of micro-organisms in favourable nutritive solutions was prevented. Of numerous substances tried, the only disinfectants which fully satisfied the above conditions were chlorine, bromine, iodine, mercuric chloride, osmic acid, and potassium permanganate; the last-mentioned only acted thoroughly in strong solutions (5 p.c.). Bromine and osmic acid are too expensive for most purposes. Mercuric chloride is very poisonous; but its action is so rapid that it could be used for solid substances, which could then be washed with water.

Mercuric chloride, thymol, amylic alcohol, and some essential oils were found effective in checking the germination of spores.

According to Koch, carbolic acid is almost without action on spores of anthrax bacilli, e.g. the bacilli spores retained their vitality after being five days in a 2 p.c. solution, and in another experiment fifteen days in a 1 p.c. solution. It is, however, destructive to the living micro-organisms themselves, for 1 gram of pure carbolic acid can completely prevent the development of anthrax bacilli in 850 c.c. of a nutritive solution, and even showed a marked effect in 1,250 c.c. Its action on other bacteria was less marked. Carbolic acid in the form of vapour did not affect the germinating power of bacilli spores at the ordinary temperature, even after being in contact with them 1½ months; but at 55°, in half an hour many of the spores were destroyed. In three hours scarcely any germinating power was discernible, whilst after five or six hours their destruction was com-

plete. Raising the temperature further did not increase the activity of the carbolic acid.

The above results were obtained with aqueous solutions of carbolic acid. Solutions in oil or alcohol did not show any antiseptic properties. This was also the case with other disinfectants, e.g. salicylic acid, thymol, &c., except when they were used with substances containing water, such as flesh, &c., when some of the disinfectant became active.

Sulphurous acid, either alone or mixed with water or steam, does not disinfect dry objects. If, on the other hand, the object is first moistened and then treated with sulphurous acid, brisk action is observed; it does not, however, destroy all germs. Its disinfecting action is thus uncertain, and it is not to be depended on.

Martens, in a prize-essay written for the medical faculty of Greifswald (C. & D. 32, 426), gives a summary of his researches upon the relative antiseptic powers of various chemical agents. His experiments were made chiefly upon the micro-organisms of pus formed on wounded surfaces, or the result of inflammation. He regards the anthrax bacillus as inappropriate to experiment upon, when the antiseptic is intended to be used for the destruction of other bacilli. The principal organisms present in pus are *Staphylococcus pyrogenes*, *aureus*, *albus*, *citrus*, and *Streptococcus pyrogenes*. Of all the disinfectants used iodine gave the greatest satisfaction, if it may be considered in the light of a germicide only, but even in most dilute solutions it is extremely irritating. A solution of 1 part of iodine in 10,000 of water proved to be powerfully active. Thymol gave satisfaction in a solution of 1:5000. From the comparatively non-poisonous nature of thymol and its great antiseptic powers, the opinion is expressed that it should occupy a more important position in surgery than it now does. Antiseptics found to be effective in dilutions of 1:1000 included solutions of sodium hypochlorite, silver nitrate (a salt which had not previously been credited with the power of preventing the formation of pus), the mineral acids (nitric, hydrochloric, and sulphuric) and mercuric chloride. The last salt has, however, been proved effective against anthrax germs when so dilute as 1:300,000. Benzoic acid was found effective in a dilution of 1:500, and salicylic acid in 1:300. The class of antiseptics effective in dilutions of 1:100 included ferric chloride, calcium hypochlorite, acid sulphate of potassium (this salt has not been recognised before as being so powerfully antiseptic), carbolic acid, potassium permanganate, quinoline, cupric chloride, acetate of aluminium, and resorcinol. The author of the essay considers that the high price of resorcinol and its action on instruments renders it an undesirable disinfectant in practice. Acetic acid and oil of turpentine were found effective at a dilution of 1:50, boric acid at 1:25, and zinc chloride at 1:20; while the class effective at 1:10 included caustic potash, acetate of copper, chloride of calcium, citrate of iron, and antipyrin. Alcohol, cadmium sulphate, lead acetate, bicarbonate of sodium, thiosulphate of sodium were effective at a dilution of 1:2, while among those bodies which were found to be wholly ineffective were the iodide, bromide, sulphate, nitrate and

carbonate of potassium, chloride and sulphate of ammonium, sulphate of magnesium, sulphate of zinc, potassium chlorate, and lime.

C. T. Kingzett has conducted several extensive series of experiments upon the comparative antiseptic values of chlorides, nitrates, and sulphates (S. C. I. 6, 702). Two series of experiments were made upon starch paste and one upon extract of beef. In the former cases, where starch paste was used, the time which elapsed before mould made its appearance was noted, using certain quantities of a 5 p.c. solution of the substances experimented with. In the latter case, where extract of beef was used, the length of time which the same 5 p.c. solution protected the extract from putrefaction was noted. From the results generally, the compounds of the alkalis and alkaline earths appeared in many instances to promote the growth of the mould in the same sort of way as Warington has observed the presence of gypsum facilitates the nitrification of urine. In no instance was the growth of mould postponed by the presence of salts of potassium, sodium, or ammonium, and among the compounds of the alkaline earths magnesium sulphate alone exhibited a slight prohibitive effect. The zinc compounds ranked with those of the alkaline earths. The sulphate of manganese in the higher proportion slightly delayed the growth of the mould. The compounds of iron, tin, lead, and aluminium exercised a distinct but not very powerful prohibitive effect, excepting the chloride of lead, the antiseptic action of which must be described as decided and as ranking with the sulphate of copper. As to copper and mercury, the chlorides of those metals rank apparently as of highest and equal value, side by side with nitrate of copper and sulphate of mercury. Somewhat below these compounds in antiseptic action stand sulphate of copper and nitrate of mercury; the first named of these substances being decidedly the more effective of the two.

With respect to the observations made with extract of meat, the results generally accorded with those of the flour-paste series, excepting that the salts of zinc appeared to exercise a distinctly superior antiseptic influence to that which they exhibited in protecting flour-paste from the growth of mould. Chloride of lead did not behave up to the expectation based upon the flour-paste experiments with that substance, but in all probability its effect is modified by the precipitation which the solution undergoes when added to meat extract. The compounds of mercury and copper again come out as most effective, and, if any choice is to be made, it seems to fall on the chlorides of those metals.

S. Bucholtz has conducted a series of experiments to determine the different amounts of each antiseptic which would check the putrefaction of a liquid of known composition. The Pasteur's liquid he used was a solution of 10 grams of common sugar, 1 gram of tartrate of ammonium, and half a gram of phosphate of potassium in 100 c.c. of distilled water. The amount of any antiseptic needed to prevent the putrefaction of this liquid was easily determined by filling a number of tubes with it, adding different amounts of the antiseptic to them, and then watching the results of their impregnation

with a few drops of a decomposing infusion of tobacco. In the following table is shown the smallest proportion of antiseptic which prevents the development of bacteria :

	1 part in
Corrosive sublimate . . . .	20,000
Thymol . . . . .	2,000
Sodium benzoate . . . . .	2,000
Cresote . . . . .	2,000
Benzoic acid . . . . .	1,000
Methyl-salicylic acid . . . .	1,000
Salicylic acid . . . . .	666
Eucalyptol . . . . .	666
Sodium salicylate . . . . .	250
Carbolic acid . . . . .	200
Quinine . . . . .	200
Sulphuric acid . . . . .	151
Boric acid . . . . .	133
Cupric sulphate . . . . .	133
Hydrochloric acid . . . . .	75
Zinc sulphate . . . . .	50
Alcohol . . . . .	50

The smallest amounts which would arrest putrefaction and render the bacteria incapable of further development when removed to fresh Pasteur's solution were found to be as follow :

	1 part in
Chlorine . . . . .	25,000
Iodine . . . . .	5,000
Bromine . . . . .	3,333
Sulphurous acid . . . . .	666
Salicylic acid . . . . .	312
Benzoic acid . . . . .	250
Methyl-salicylic acid . . . .	200
Sulphuric acid . . . . .	161
Cresote . . . . .	100
Carbolic acid . . . . .	25
Alcohol . . . . .	4.5

In a memorandum appended to the report of the medical officer to the Local Government Board, Dr. J. Burdon Sanderson (Ph. J. [3] 18, 993) states that hitherto attention has been mainly directed to the rendering of solid and liquid excreta innocuous, but he urges that this is not by any means all that can be accomplished by the application of chemical agents for the prevention of infective diseases. He points out that the innate no less than the extraneous contagia have a life history which is made up of two states of existence, alternating with or succeeding each other; one in which they vegetate with more or less activity in the external environment, the other in which they have their abode in the living blood or tissue, exerting there their hurtful function, and that the problem of disinfection relates to the latter as well as to the former of these states.

Dr. Sanderson considers that the most important lesson that has been learnt in recent researches respecting the nature of contagia is best expressed in the word 'specificity,' by which he means that each individual kind of contagium has a power peculiar to itself of producing a particular modification of the chemical processes which constitute the life of the organism it attacks. Very little is yet known respecting the effect of chemical agents upon the product of such modifications within the organism, and before much extension of this knowledge can be hoped for not only will a more intimate acquaintance with the contagia be indispensable, but the

nature of the modification produced by each will require to be worked out. Holding these views, therefore, Dr. Sanderson indicates four lines of research which should be followed with a view of acquiring a better and more practical knowledge of the art of disinfection: (1) The disinfection of solid and liquid excreta and of clothing; (2) the disinfection of air; (3) the detection of contagia in food, air, or water; and (4) the use of colytic agents with a view to the inhibition of infective action within the living body.

**Internal disinfectants.** Antiseptics can be employed externally without regard to anything beyond their power to destroy microbes; but in certain diseases it is very desirable to bring disinfectants in actual contact with the stomach and intestines, and in such cases the primary or secondary effects they may produce on the system must be carefully considered. When the contents of the stomach are undergoing decomposition either from yeast, sarcinae, or bacteria, good results are obtainable from the administration of phenol or creosote, because these substances come into direct contact with the microbes, and will be effective in quantities too small to be injurious to the patient. If the intestine is to be disinfected, a remedy less soluble and poisonous and less readily absorbed than phenol or creosote should be chosen. Thus salol passes through the stomach unchanged, but in the duodenum is split up by the pancreatic juice into phenol and salicylic acid. Here the phenol is liberated at the desired point, but its action is too violent, and hence betol seems a preferable remedy to salol, for the  $\beta$ -naphthol produced by its decomposition is less soluble and poisonous than phenol, while more powerfully antiseptic. Resoreinol, thymol, and sodium benzoate are other intestinal disinfectants which are sometimes useful, though more or less open to the same objections as phenol. The phenol-sulphonates, such as sulpho-carbolates and aseptol, though less powerful disinfectants than carbolic acid, are far less poisonous and are of considerable value as intestinal disinfectants. The diphenyl derivatives appear to have less toxic action, and at the same time to be more powerfully antiseptic, than those containing a single phenyl group (Lauder Brunton, Ph. J. [3] 19, 1066).

#### HALOGENS.

The disinfectant and deodorising characters of the free halogens are well known. Their deodorising value depends largely on their power of reacting with sulphuretted hydrogen, with separation of sulphur and formation of a hydracid. Their value as disinfectants depends on their power to break up ammonia and other volatile bodies produced in putrefaction and decomposition, together with their powerful oxidising properties. In other words, their value depends mainly on their affinity for hydrogen and their power as oxidisers which is the result of such affinity.

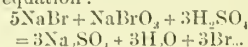
Professor Cash, as the result of experiments instituted to ascertain the relative potency of chlorine, bromine, iodine, and sulphurous acid in destroying the contagia of anthrax and tubercle, concluded that, when employed in solu-

tions of a strength proportional to their atomic weights, the three halogens did not present any very remarkable differences in their disinfecting power, though chlorine appeared to be the most potent and iodine the least. Cash found that the halogens failed to exercise any disinfectant influence when employed in any dilute solution, even when the virus to be destroyed was exposed to their action for a very long time. He gives the preference to the halogens and sulphurous acid in the form of solution, and if it be necessary to employ the agent in the gaseous state, considers sulphur dioxide preferable to the halogens.

**Chlorine** is commonly liberated from *bleaching-powder* by the action of aerial carbonic acid or the direct addition of acetic, hydrochloric, or sulphuric acid. When a weak acid is used, such as acetic or carbonic acid, and an excess avoided, *hypochlorous acid* ( $\text{HClO}$ ) may be liberated instead of free chlorine. This is probably quite as efficacious as chlorine itself. The *oxides of chlorine* evolved when potassium chlorate is treated with a mineral acid are sometimes employed for disinfectant purposes.

In using chlorine and similar agents, the fact is often overlooked that in the destruction of any disease-producing material by a disinfecting agent it is necessary to take into account the extent to which the disinfectant is used up by harmless material. Consequently, to ensure efficiency, the quantity of disinfectants used should be proportioned not only to the amount of morbid material to be destroyed, but also to the amount of harmless material with which it may be associated.

**Bromine** has powerful disinfectant properties, having, according to Koch, a greater capacity than chlorine for destroying micro-organisms, though this conclusion is not confirmed by the experiments of Cash on the action of the halogens on the contagia of tubercle and anthrax. A useful mixture for generating bromine gradually is the preparation known as *Bromidine*. This mixture of a bromide and bromate yields free bromine when treated with an acid, according to the equation:



A mixture of a bromide and bromate in the proper proportions results from the treatment of bromine with a solution of carbonate or hydroxide of sodium. If the product be evaporated to dryness, and mixed with a suitable quantity of acid sulphate of sodium ( $\text{NaHSO}_4$ ), the preparation will evolve bromine slowly as it gradually absorbs moisture from the air, or more readily if water be actually added.

**Iodine** is regarded by Koch as less powerful in its antiseptic properties than either bromine or chlorine, but his conclusions, though probably correct, are open to the objection that the iodine was employed in alcoholic solution and the bromine and chlorine in aqueous. Various forms of lamp have been devised for the gradual volatilisation of iodine and the diffusion of its vapour, or the finely divided particles produced on condensation, through the atmosphere to be disinfected.

Casson and Brownen (Med. Press and Circular, Oct. 5, 1887) have proposed to use candles



containing iodine and salicylic acid for the purpose of diffusing disinfectant and deodorant vapours in sick chambers. The iodine combined with salicylic acid can, they state, be perfectly incorporated with fats, paraffin, or wax, and that when such candles are burnt they evolve iodine and phenol in a vaporous form. The phenol is divided from the decomposition of the salicylic acid, and its presence can be demonstrated by the formation of trinitrophenol, or picric acid, upon passing the products of combustion through nitric acid. If the combustion goes on too freely and completely, the decomposition is more thorough and no phenol is evolved. The iodine is simply volatilised, and its presence in the products of combustion can be detected by its action on starch mucilage. These candles are said to speedily remove the smell of tobacco or sulphuretted hydrogen, and the vapours have been found of value in cases of asthma, hay fever, and spasmodic cough.

*Iodine trichloride*,  $\text{ICl}_3$ , forms long, lemon-yellow crystals which readily undergo dissociation, especially at a temperature above  $25^\circ\text{C}$ ., with formation of chlorine and iodine monochloride. The smell is irritating and at once suggestive both of iodine and chlorine. The aqueous solution of iodine trichloride undergoes gradual decomposition, and the alcoholic solution more rapidly.

According to Von Langenbach, iodine trichloride is one of the most powerful germicides known. An aqueous solution containing 0.67 to 1.00 gramme per litre is as powerful as a 4 per cent. solution of phenol, can be used for washing hands and instruments, and may be given internally. Sixty drops of a solution of 1 in 1200, given every two hours, has been found of value in dyspepsia arising from bacteria. The spore-killing power of iodine trichloride is said to be second only to that of mercuric chloride.

**Fluorine.** For obvious reasons the disinfectant value of fluorine and its simpler compounds have not been studied, but the value of the fluosilicates for the purpose has been recognised by Wm. Thomson, and their use as disinfectants patented by him. The fluosilicate (silicofluoride) of sodium,  $\text{Na}_2\text{SiF}_6$ , is the form commonly used, and is now an article of commerce under the title of *Salufer*. It forms a white, odourless powder, sparingly soluble in water. The aqueous solution possesses but a slight saline taste, and, as it is non-poisonous, seems well suited for preserving articles of food. A saturated solution contains 0.61 p.c. of the salt, and can be applied to a wound without producing irritation.

#### ORGANIC HALOGEN COMPOUNDS.

**Chloroform.** The vapour of chloroform has proved to be of considerable service as an antiseptic, and many almost startling results have been obtained.

Dr. Richardson reports (*Lancet*, Nov. 25, 1882) that a piece of fresh lung was placed in a vessel so arranged that the lung was completely surrounded by the vapour of chloroform; the specimen was then preserved for a period of thirty-five years. Vegetable as well as animal tissues can also be preserved with chloroform vapour in a most satisfactory manner—fresh

digitalis leaves having been preserved for three years in this way (*Ph. J.* 18, 356). An entire specimen of *Alisma plantago* has been preserved for about two months in an atmosphere of chloroform; it is true that the specimen became somewhat flaccid, but beyond this very little change was perceptible.

**Iodoform**  $\text{CHI}_3$ . Much conflict of evidence exists as to the antiseptic properties of iodoform. De Ruyter (*Med. Press*, Oct. 26, 1887, 403) confirms the statement that outside the body, whilst undecomposed, iodoform exercises no antiseptic action, but in the presence of pus at the temperature of the body the iodoform undergoes decomposition. This appears to be due to the influence of the pus cocci, since sterilised blood or blood-serum was found to induce no chemical change in iodoform. Dr. De Ruyter says that the iodine liberated by the breaking up of the iodoform combines with ptomaines present, depriving these of their harmful properties, but leaving the cocci alive, though much reduced in activity.

Mosetig (*Medical Record*, July 1887) has employed iodoform with success, and without bad concomitant effects, in the treatment of severe burns or scalds. He considers the action both analgetic and antiseptic, and employs an ethereal solution of iodoform to saturate purified gauze, which when dry is used for dressing the burn and covered with gutta percha tissue and cotton wool.

**Iodol.** The tetraiodo-derivative of pyrrol has been recommended as a substitute for iodoform, as it is devoid of the pungent odour of the latter compound and is said to be quite equal to it in antiseptic value.

#### BORON COMPOUNDS.

**Boric acid**  $\text{H}_3\text{BO}_3$  is largely used as a preservative of food. Like borax it has gained favour because of its harmless character, which particularly adapts it for food preservation. Fish have been preserved on a large scale by means of boric acid, and with very satisfactory results. The dry boric acid is placed in very thin alternate layers between the fish in barrels. It is also used in solution for the same purpose, both methods being still in use, in Sweden particularly.

As an antiseptic dressing for wounds &c. boric acid has gained favour on account of its non-poisonous nature and the fact that 5 p.c. solutions can be used without causing irritation to the most delicate surfaces.

The varying influence of boric acid upon different fermentations has been investigated by Herzen. He finds that the conversion of starch into glucose by the ordinary or pancreatic ferment is not influenced by boric acid, even when the menstruum is a saturated solution.

The conversion of glucose into alcohol appears to be favoured by the presence of boric acid, even in small quantity; but the presence of boric acid in minute quantity almost prevents the conversion of alcohol into acetic acid. So also, in respect to the fermentation of albuminoid bodies this acid shows a marked difference in its action. The conversion of albumen and fibrin into peptone and tryptone by means of pepsin and trypsin is much accelerated by it,

whilst putrefactive fermentation is entirely prevented.

**Boroglyceride** has the constitution of a glyceryl borate  $(C_3H_5)_3BO_3$ , and is prepared by heating 3 parts of glycerin to about  $160^\circ C.$ , with 2 parts of boric acid. According to Sulman and Berry, the commercial product contains only about 25 p.c. of glyceryl borate, with 75 p.c. of free boric acid and glycerin in equivalent proportions. Moreover, when the true glyceryl borate is treated with water it suffers immediate hydrolysis into boric acid and glycerol, and hence the antiseptic value of the preparation would appear to be simply dependent on the 45 to 50 p.c. of boric acid liberated on use.

**Borax** acts as a somewhat powerful antiseptic, and, on account of its comparatively non-poisonous nature, it has been used largely for preserving food. Borax in the proportion of 1 lb. to 100 gallons of milk has been used as a preventive of decomposition during the summer months, when milk is prone to change, and it has undoubtedly a powerful action, for it is quite possible to keep milk sweet for from 3 to 4 days, in the height of summer, under such conditions.

'*Glacialin salt mixture*' and '*Glacialin rose extract*' are both mixtures of boric acid with borax, the latter mixture being intended to preserve meat without altering its colour.

#### SULPHUR COMPOUNDS.

**Sulphurous acid (sulphur dioxide).** The burning of sulphur for the purpose of disinfection dates back for a considerable time. Sulphurous acid is perhaps one of the most satisfactory germicides. Its power has been somewhat overrated, but it is, nevertheless, when used in the most advantageous manner, both thorough and rapid in its action.

The Committee on Disinfectants of the American Public Health Association, in a preliminary report, state that to insure perfect disinfection a weight of 3 lbs. of sulphur should be burnt for each thousand cubic feet of air, and this proportion ought certainly to form the minimum limit of sulphur used. When *dry*, sulphur dioxide does not appear to have nearly so powerful a germicidal action as when moist. It is therefore wise to boil away a large quantity of water in a closed room previous to disinfection, by these means securing solution of the gas on the surface of the walls, &c., as well as in the atmosphere itself. Unfortunately, it is quite impossible to disinfect a sick chamber by means of sulphur dioxide, for even a small proportion renders the air irrespirable, and it induces coughing when only existing as traces in the air.

Arloing, Cornevin, and Thomas concluded from experiments made at Lyons, on the influence of various disinfectants upon the virus of symptomatic anthrax, that sulphur dioxide has no effect upon the fresh virus of anthrax. S. Schönland (Annals of Botany, November 1887, 178) makes use of sulphurous acid for preserving the colours of plants and preventing the ravages of insect-life afterwards.

According to Koch, sulphurous anhydride has little or no action unless the articles treated were first moistened, and even then his results

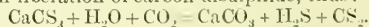
went to prove that it was not satisfactory with all kinds of germs.

**Thioeamf.** When camphor is exposed to sulphur dioxide it absorbs an enormous volume of the gas and forms a liquid which has been introduced under the name of 'thioeamf' (Chem. News, 59, 291). It can be preserved without pressure in well-closed bottles, but when exposed to the air evolves much sulphur dioxide, the contents of a six-ounce bottle being said to furnish more than 20 litres of the gas.

**Metallic sulphites** have marked antiseptic properties. Sodium sulphite has been long employed for preserving tinned foods, for which purpose its power of absorbing oxygen is also of value. The sulphites of calcium and magnesium are insoluble, or nearly so, in water, but dissolve in a solution of sulphurous acid forming so-called 'bisulphites,' which are extensively employed for preserving beer.

**Carbon disulphide,  $CS_2$ ,** possesses powerful antiseptic properties. It is soluble in water to the extent of 2 or 3 parts per 1,000 at the ordinary temperature, and Ckiandi Bey (C. R. 99, 509) finds that the solution arrests all fermentation, kills microbes, and is a most energetic antiseptic. He recommends the use of the solution internally in cholera and all zymotic diseases, and the experiments of Dujardin Beaumetz show that when employed in typhus the diarrhoea is arrested, the stools disinfected, and the breath sweetened. For medicinal use the commercial carbon disulphide must be purified by agitation with metallic mercury till a black precipitate is no longer produced.

**Thiocarbonates** possess antiseptic properties in consequence of their gradual decomposition with liberation of carbon disulphide, thus:—



Commercial thiocarbonates are very variable in quality, and hence Falières has devised the following simple method of assaying them: 10 grammes' weight of the sample is placed in a graduated cylinder holding 50 c.c., and 10 c.c. of water and 10 c.c. of benzene are then added. After mixing well, 20 c.c. of sodium bisulphite solution of 1.32 sp.gr. is added to the contents of the cylinder and the whole well shaken. After about an hour about 10 c.c. of ammonia should be added, and the mixture again shaken and allowed to stand for a short time. The carbon disulphide produced by the decomposition of the thiocarbonate dissolves in the benzene, and the quantity can be ascertained by noting the increase in the bulk of the layer of the latter; 1 c.c. of carbon disulphide weighs about 1.27 grammes at the ordinary temperature.

**Xanthates (ethyl-thio-oxycarbonates)** have received application for destroying the *phylloxera* which affect the vine. Their action is probably due to the liberation of xanthic acid  $CS \begin{cases} O.C_2H_5 \\ SH \end{cases}$  and the decomposition of this with formation of carbon disulphide.

#### HYDROGEN PEROXIDE.

The unstable nature of hydrogen peroxide renders it a powerful oxidising and deodorising agent, as it immediately re-acts with and destroys sulphuretted hydrogen, and many other

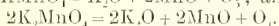
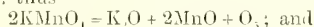
compounds susceptible of change. It possesses the advantage, sometimes a very important one, that the product of its decomposition (water) is neutral and destitute of chemical activity, while hydrogen peroxide itself has not the extreme tendency to act on inert organic matter which so much diminishes the practical value of the permanganates. On the other hand, hydrogen peroxide possesses true disinfectant properties of a marked character. According to P. Bert and P. Reynard (Berl. Ber. 15, 1585), all fermentations due to organised ferments are at once arrested by hydrogen peroxide, and the ferment is killed, while no effect is produced on soluble ferments (*e.g.* ptyalin, pepsin, diastase, pancreatin). Fibrin decomposes hydrogen peroxide, but when dissolved in hydrochloric acid, or changed into fibrin-peptone by artificial digestion it is without action. Egg-albumin, casein, milk, urea, fats, saliva, starch, and fruit juice are also stated to be without action on hydrogen peroxide.

*Sanitas* is a commercial preparation, owing much of its disinfectant value to the presence of hydrogen peroxide. It is prepared by blowing air through warm oil of turpentine in contact with water. Under these circumstances an aqueous liquid ('*sanitas*') is obtained, containing hydrogen peroxide, camphoric acid, and certain other oxidation-products of the turpentine; while the residual oil itself possesses disinfectant value. Aqueous *sanitas* contains hydrogen peroxide in quantity corresponding to an evolution of twice its volume of oxygen when decomposed. The disinfectant properties of *sanitas* have been studied very completely by its inventor, C. T. Kingzett.

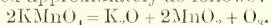
#### PERMANGANATES AND MANGANATES.

These salts are well known as disinfectants, and have obtained deserved favour. A great objection to their use is the facility with which their oxidising power is wasted on inert matter.

In presence of a free acid (*e.g.* sulphuric, hydrochloric) the permanganates yield 5 atoms of available oxygen, while the manganates furnish 4 only: thus



In the absence of free acid, permanganates are reduced approximately as follows:



Potassium permanganate is the best-known salt of the series. The sodium salt exists in Condé's fluid, and the *permanganates of calcium, zinc, and aluminium* have also met with a limited use as disinfectants. The last-named salt is prepared by H. B. Condé by treating a strong hot solution of aluminium sulphate with solid potassium permanganate. The mixture is allowed to cool, when potash-alum crystallises out, and aluminium permanganate and sulphate remain in solution.

*Condé's crimson disinfecting fluid* is an impure solution of sodium permanganate  $\text{NaMnO}_4$ , while the active constituent of the green fluid is chiefly sodium manganate  $\text{Na}_2\text{MnO}_4$ , though a small but variable amount of permanganate is also present, and may be detected by precipitating the liquid with barium chloride and filtering through asbestos, when the manganate being

removed the crimson colour of the permanganate becomes apparent. Condé's green fluid is strongly alkaline, the crimson nearly neutral. The latter contains much sulphate, evidently due to the sulphuric acid employed to neutralise the excess of alkali in the crude product. Samples of Condé's green and crimson fluid analysed by A. H. Allen in 1871 (Year-book of Pharmacy, 1871) were found to contain:

	Green	Crimson
Available oxygen (in grammes per litre)	3.883	3.921

The available oxygen was determined by titration with standard oxalic acid in presence of sulphuric acid.

*Hartman's crimson salt* consists of a mixture of permanganates or permanganates with other substances, the preferable mixture being (according to patent 9,538, 1884): potassium permanganate, 1 part; potash alum, 8 parts; borax, 1 part; and common salt, 6 parts.

A mixture of an alkaline manganate with sulphate of magnesium, calcium, or zinc, or with boric acid, has been patented by Dupré and Hake, while Stevenson and Tatters have patented a mixture of sodium manganate with about half its weight of bleaching powder.

#### ALUMINIUM SALTS

have a limited antiseptic power. An impure chloride was met with in commerce some years since under the title of 'Chloralum.' The sulphates of aluminium have been recommended by Wade (Pharm. Record, Nov. 1, 1888) as non-poisonous and non-irritating antiseptics. The thiosulphate has also been recommended. The preservative properties of *alum* are well known.

#### SALTS OF THE HEAVY METALS.

Many of the compounds of the heavy metals have obtained more or less favour as disinfectants. In many cases they are little more than deodorisers, which property they possess chiefly through their power of fixing sulphuretted hydrogen and ammonia. In other cases they possess antiseptic properties through their power of coagulating and forming insoluble compounds with albumin. In a few cases the salts of the heavy metals act as well-defined disinfectants of a powerful character, this property being, in some cases at least, due to their marked poisonous properties.

Of the compounds of the heavy metals, the following have received most application in the direction in question.

**Zinc chloride.** A solution of this compound is known in commerce as Burnett's disinfecting fluid.

Dr. Koch has pronounced chloride of zinc to be practically inert as a germicide; but, although it may not be directly poisonous to germs, Dr. Hamilton believes that it is capable of rendering a cut surface a barren cultivation-ground, and infers that it will produce a similar effect on the walls of an abscess. This view is supported by the experiments of Dr. Richardson, which prove that a body may be embalmed perfectly by means of chloride of zinc and spirit. It is still the practice to embalm bodies in the south of Europe by a process in which chloride of zinc is used as the antiseptic.



Ferric chl-ride and ferrous sulphate have little value other than as deodorisers.

Cupric sulphate, formerly used for preserving timber, is now superseded by creosote, not, however, because it was found inefficient as a preservative, but because it soon washed out of the wood.

Stannous chloride is said to be at least as good as most other metallic salts, and to have the advantage of not acting on lead or iron pipes. This character would be true only of a neutral solution.

Mercuric chloride has a disinfectant value of the highest kind. It is probably the most powerful and certain germicide known, but, like all metallic salts, is only active when in actual contact with the substance. Solutions of 1:1,000 to 1:10,000 of mercuric chloride have long been used for surgical operations, and are now employed by dentists as an antiseptic dressing prior to filling teeth. Koch concluded, from an elaborate series of experiments, that the most valuable *true disinfectants* (i.e. reagents capable of destroying micro-organisms) available for practical purposes are chlorine, bromine, and mercuric chloride; while the most potent antiseptics are mercuric chloride, certain ethereal oils, and allyl alcohol.

Mercuric cyanide and oxycyanide have a high antiseptic value, and for some purposes present advantages over the chloride. Solutions of the oxycyanide have a slight alkaline reaction, and precipitate albumen but slightly. A solution of 1 in 1,500 does not seriously attack the metals of surgical instruments, and is tolerated well by the mucous membrane and by wounds. Added to peptonised broth, Chibret (C. R. 107, 119) found mercuric oxycyanide to have an antiseptic power six times as great as that of the chloride, but in its effect on *micrococcus aureus* it was somewhat less powerful than mercuric chloride. It has been found of great service in diphtheria (Lancet, March 24, 1888, p. 591).

Mercuric salicylate is referred to under the head of *Salicylic acid*.

#### PHENOLS.

A number of the most important antiseptic agents contain phenol or a phenoloid body as the active constituent, or owe their efficacy to the ease with which they suffer decomposition with formation of a phenol. In fact, the majority of bodies containing the phenyl group possess antiseptic properties.

Carbolic acid has taken for a number of years a leading place among antiseptic disinfectants. The best qualities of the commercial product may be regarded as chemically pure and absolute phenol,  $C_6H_5.OH$ . The highest grade melts at  $40.2^\circ C.$ , and is free from homologues, the proportion of which gradually increases in the lower qualities. Thus 'Calvert's No. 5 carbolic acid' is fluid at ordinary temperatures and consists chiefly of cresylic acid (isomeric cresols  $C_8H_9.OH$ ), with smaller proportions of still higher homologues and traces of naphthalene and other impurities. Still lower qualities of commercial carbolic acid contain notable quantities of hydrocarbon oils, and it is not unusual

to mix carbolic acid with an equal weight or more of naphthalene oils or similar products to meet the exigencies of the market.

For ordinary disinfecting purposes an article consisting mainly of cresylic acid and higher homologues appears to be fully as serviceable as pure carbolic acid, but according to Dr. C. M. Tidy the value does not extend to the lime compound of cresylic acid, which is said to be practically valueless as a disinfectant, whatever may be the value of the carbolic compound with lime. It is probably correct that both carbolic and cresylic acid have little or no antiseptic value when absorbed in a large excess of slaked lime, but the neutral carbolate and cresylate of calcium will undergo decomposition by aerial carbonic acid and hence will act as gradual disinfectants.

Carbolic acid acts as a caustic on the skin, and is powerfully poisonous. It appears to act on the system locally by coagulating albumin, and generally by paralysing the nerve-centres. According to C. Lowe, the effect of even momentary contact of the strong acid with any considerable surface of the lower part of the body is apt to be fatal, but it has often been applied to the arms with comparative impunity. M. Gosselin has made a series of investigations bearing more particularly upon the action of phenol when placed upon the living body, as in surgical dressings and operations (Ph. J. [3] 14, 242). Working with solutions of different strength, containing from 1 to 5 p.c. of carbolic acid dissolved in alcohol, dilute alcohol, and also camphorated spirit, he applied the antiseptic to a transparent membrane through which the blood was circulating. He states that the circulation of the blood in the capillaries is arrested, more or less quickly, and in direct proportion to the strength of the solution. He considers that the most probable explanation of this is that the blood becomes coagulated as soon as the antiseptic has traversed the delicate membrane and comes in actual contact with it. This action, according to M. Gosselin, can be strictly compared with that of a caustic, and he is of opinion that phenol applied in this manner first acts as a germicide and then as a semi-caustic or astringent.

Although the term 'carbolic acid' has been extended commercially so as to include products consisting chiefly of cresol and still higher homologues of phenol, it appears a straining of its legitimate signification to apply it to products from which the real carbolic acid has been previously extracted. This, however, is sometimes done, and 'carbolic acid' and 'carbolic powders' are sold in which real carbolic acid is conspicuous by its absence. But if the inexact description of cresylic acid as carbolic acid is objectionable, the matter becomes more serious when the article is purposely mixed with neutral tar oils, or other hydrocarbons of little direct value as antiseptics. This has been done, in certain cases, to the extent of 50 p.c., the 'carbolic acid' and 'carbolic powders' sold to corporations and local boards of health affording a fertile field for the operations of the blender.

The carbolic or cresylic acids from coal tar are sometimes completely or partially replaced by the mixture of phenoloid bodies obtained from the tar or oil produced by condensing the waste

gases from blast-furnaces burning bituminous coal.

**Blast-furnace creosote oil** is now produced in enormous quantities in Scotland, and has already found an extensive application for creosoting timber, or producing the 'lucigen' and 'luminator' lights, and as a liquid fuel. It contains from 20 to 35 p.c. of phenoloid bodies soluble in caustic soda, as against 5 to 10 p.c. in coal-tar creosote oil of London make (Newcastle coal). Blast-furnace creosote oil affords a cheap and abundant source of phenoloid bodies, which appear to be fully equal to the coal-tar acids in antiseptic value.

Watson Smith (S. C. I. 2, 497) found a sample of the phenoloids extracted from blast-furnace tar to contain only 1.33 p.c. of real phenol boiling at 182°C., whereas the tar acids from Lancashire coal-tars yield about 65 p.c. of crystallisable carboic acid. The fraction which would contain the cresols (cresylic acid) amounted to 4.5 p.c. of the total phenoloids. The larger fractions (19.4 p.c.) distilling between 210° and 230° probably consisted mainly of phlorol (mixture of the xylenols,  $C_8H_9(OH)$  and cresol  $C_6H_3(CH_3)_2(OH)(O.CH_3)$ ). A large proportion of the phenoloids distilled at a temperature above 230°, but their nature requires further study. The fraction distilling above 350° gave, on treatment with soda and exposure to air, unstable colouring matters which are probably allied to the eupitonic acid obtained from wood-tar.

These results show that a certain similarity exists between the phenoloids of low temperature tars, whether they be obtained by the distillation of wood or shale, or by the condensation of gases from blast-furnaces, coke-ovens, or gas-producers.

On *prima facie* grounds we should expect the phenoloids of blast-furnace tar to have a high antiseptic value. It was to the phenoloids of wood-tar that Reichenbach in 1832 first applied the name of creosote or 'flesh preserver.' When, soon after, Runge discovered carboic acid in coal-tar, it was confused with the wood-tar principle, and it is probable that the antiseptic properties of carboic acid itself would not have received such prompt and wide recognition but for the advantage it derived from its confusion with the original wood-tar creosote of Reichenbach. In short, wood-tar creosote has been superseded by the cheaper product from coal-tar except for certain limited applications.

**Neosote.** The phenoloids of blast-furnace tar are now an article of commerce under the name of Neosote ('new preservative'). They are obtained by treating the creosote oil with caustic soda, and decomposing the solution of the soda-compound thus obtained, after separating the insoluble hydro-carbon oils, by the waste gases from the blast-furnaces. The carbonic acid in these converts the soda into carbonate and the phenoloids are set free. The solution of sodium carbonate is causticised with lime, and thus furnishes caustic soda for treating a fresh quantity of the creosote oil. The crude phenoloids are redistilled, the distillate furnishing the 'Neosote' of commerce. It contains only 1 or 2 units p.c. of crystallisable carboic acid, a large proportion of cresols, and gradually decreasing proportions of the higher homologues.

Oxyphenols, similar to or identical with those of wood creosote, are also present, but the method of purification adopted eliminates a large proportion of these constituents. When freshly distilled, neosote is almost as colourless as water, but it acquires a dark yellow or brown colour by keeping. Experiments made to test the antiseptic value of neosote have shown that it is fully able to compare with crude carboic acid, while its caustic properties (when applied in a concentrated condition to the skin) appear to be much less marked than those of the gas-tar product.

**Assay of carboic acid.** In cases where carboic acid is largely adulterated with hydro-carbon oils (*e.g.* naphthalene oils), the proportion present may be ascertained by introducing 10 c.c. of the sample into a graduated tube and adding gradually, noting the effect produced, 20 c.c. of a solution of caustic soda, free from alumina, containing 9 p.c. of NaHO. The tube is then closed and the contents well agitated. If the sample contain a considerable proportion of hydro-carbon oils, the phenols will be completely dissolved by the alkali, while the neutral oils will form a separate stratum above or below the other, according to their density. A volume of petroleum spirit equal to that of the sample used may now be advantageously added. Its employment facilitates the separation of the oily stratum, and renders the reading of its volume more easy and accurate. Of course the volume of petroleum spirit used must be deducted from that of the total oily layer. The quantity of soda prescribed above is not sufficient to combine with 10 c.c. of phenols, and hence in the case of carboic acid of fair quality the measure of alkaline solution must be increased to 30 or 40 c.c. This plan is preferable to using a stronger solution, which is apt to retain hydro-carbons in solution. In fact, phenate of sodium dissolves both hydrocarbons and phenols. The method just described is often useful as a rough test in works where the general quality of the carboic acid is known, but where a more accurate determination of the neutral oils is required the following method should be employed: A known quantity of the crude carboic acid (preferably 100 c.c.) is distilled to the point of pitching, and the whole of the distillate agitated with soda solution. The alkali should at first be of moderate strength (sp.gr. 1.125), but the operation should be repeated with fresh quantities of soda solution of 1.34 sp.gr. until the extraction is complete, as shown by the separation of mere traces of tar-acids on acidifying the alkaline liquid. To cause the alkaline liquid to separate completely and promptly from the stratum of neutral oils, an addition of petroleum spirit should be made and the whole well agitated. The petroleum spirit acts as a solvent for the oils and also prevents the naphthalene from solidifying or being partly dissolved by the alkaline liquid. The two layers are then separated and the tar acids liberated in a flask with a long narrow graduated neck, mercury is then run in until the zero mark is reached. This method is decidedly preferable to that of liberating the tar acids in a cylinder. It must be borne in mind that the tar-acids separated are not anhydrous.

The specific gravity of crude carbolic acid at the ordinary temperature should be between 1.050 and 1.065. If lighter than this it is suspicious. In presence of light tar oil, the density is often as low as 1.040 or 1.045.

For the estimation of the *water* in crude carbolic acid, Bach agitates the sample with half its volume of a saturated solution of common salt. The loss of volume experienced by the carbolic acid shows the measure of water present. If the experiment be made in a burette furnished with a glass tap, the saline solution can be run off and the phenolic layer treated with soda solution as already described. Other methods have been described by Beckurts, Schliekum, Salzer, and Vulpinus (J. C. S. 50, 1081). The inferior grades of carbolic acid contain the smallest proportion of water.

The following method of assaying crude carbolic acid with a view of ascertaining its quality, and the approximate proportion of *crystallisable phenol* contained in it, is due to Charles Lowe, and is said to be largely employed by manufacturers:—1,000 grains or 100 c.c. measure of the sample is placed in a retort (without any special condensing arrangement) and distilled, the liquid which passes over being collected in graduated tubes. Water first distils, and is followed by an oily fluid. When 10 p.c. by measure of the latter has been collected, the receiver is changed. The volume of *water* is then read off. If the oily fluid floats on the water, it contains *light oil of tar*. It should be heavier than water, in which case it may be regarded as hydrated acid containing about 50 p.c. of real carbolic acid. The next portion of the distillate consists of anhydrous acid, and when it measures 62.5 p.c. the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 62.5 p.c. of anhydrous acid contains variable proportions of carbolic and cresylic acids. These may be approximately determined by ascertaining the solidifying point, which should be between 60° and 75° F. (15.5° and 21° C.). Having ascertained this temperature, a mixture of pure carbolic and cresylic acids is made in such proportions as to have the same solidifying point. This may be adjusted by trial, or a series of standard specimens may be prepared. The exact point of solidification can be more sharply read if a minute fragment of crystallised carbolic acid be added to induce the commencement of the change of state; or the sample may be solidified, and the liquefying point noted.

Many qualities of crude carbolic acid now contain a comparatively small proportion of light oils (5 to 6 p.c.), and hence a notable quantity of carbolic acid is lost in the 10 p.c. first distilled. This raises the proportion of cresylic acid in the 62.5 p.c. next collected, and hence a product is obtained having too low a solidifying point. A preferable plan of assaying the second and third qualities of carbolic acid would probably be to reject all that passes over below 185°, then distil to 190° or 195° and take the measure and solidifying point of this fraction. For No. 1 quality, with 62.5 p.c. of distillate crystallising above 70° F., only the portion passing over below 180° to 182° should be rejected.

About 12 p.c. of water usually passes over from this kind of acid, though the proportion ranges from 10 to 17 p.c., and at times 10 p.c. of neutral oils are present. By stipulating that a sample should contain a certain proportion of anhydrous phenol (exclusive of neutral oils as estimated by soda) distilling below a given temperature and having a definite solidifying point, a more accurate knowledge of the product would be obtained. Or the quality of the sample might be simply expressed in units of anhydrous phenols solidifying at a certain fixed temperature.

The mixtures of phenols from shale-tar and blast-furnace creosote are liable to be sold for crude carbolic acid from gas-tar. This substitution can be detected by a modification of Hager's glycerin test: on treatment with 3 measures of 75 p.c. glycerin the greater portion remains undissolved, while carbolic acid, particularly in the absence of neutral tar oils, would be dissolved on repeated shaking with the diluted glycerin. If the small quantity of phenol dissolved by the glycerin from shale-tar and blast-furnace creosote be extracted by chloroform, and the latter allowed to evaporate spontaneously, the residue will give the reactions of carbolic acid fairly perfectly. The colouration with ferric chloride, however, changes from violet-blue to brown instead of remaining permanent, as is the case when crude carbolic acid from gas-tar is treated in the same manner.

**Carbolic Powders.** A variety of disinfecting powders are now made which owe their efficacy chiefly to the fact of their containing more or less crude carbolic acid. In some cases the basis of the powder is slaked lime, but the resultant 'carbolate of lime' is of little value for antiseptic purposes. A number of substances besides lime have been employed and patented as absorbents of carbolic acid for the manufacture of carbolic powders. Thus 'MacDougall's disinfecting powder,' the oldest preparation of the kind, is made by adding a certain proportion of crude carbolic acid to a crude sulphite of calcium, prepared by passing sulphurous acid gas over ignited limestone. Sulphurous acid is introduced into other powders by the direct addition of a solution of calcium b.sulphite, and the use of other sulphites has also been patented. 'Calvert's carbolic acid powder' is made by adding carbolic acid to the siliceous residue resulting from the manufacture of sulphate of aluminium or patent alum, from shale or kaolin. Calcium sulphate is likewise a suitable absorbent, and kieselguhr has been patented by C. Lowe for the stronger powders. Good ordinary carbolic acid powders contain from 12 to 18 p.c. of carbolic acid. As much as 50 p.c. is absorbed by kieselguhr. The use of peat as an absorbent of carbolic acid has been patented by West-Knights and Gall, while Allen and Angus have patented the use of blast furnace slag as an absorbent. Limestone is also used as a base, and spent gas-lime has been patented by Austin. A mixture of bleaching powder and phenol recently received protection. MacDougall Bros. have patented the use of soluble salts as absorbents of carbolic acid, the resultant powder being more readily removed and less liable to choke up drain-pipes than the preparations commonly employed.



A step in the same direction is the patented preparation called *borophenol*, which is made by absorbing carbolic acid in dried borax.

*Assay of carbolic powders.*—The relative antiseptic values of different carbolic powders is best determined by incorporating a definite amount of each sample of powder with some putrescible liquid or semi-liquid substance, keeping each set of experiments in the same atmosphere as far as possible, and noting the number of hours or days which elapse before decomposition takes place. Amongst the most suitable putrescible substances to experiment upon may be mentioned fresh urine, a somewhat weak nutritive gelatin, and beef-tea, filtered whilst warm. When liquids are worked upon, a microscopic search for bacteria should be made at intervals of 12 to 24 hours.

For the determination of the percentage of crude acid contained in siliceous carbolic powders, a method frequently used is to introduce 1,000 grains or 100 grams of the powder into a tubulated glass or copper retort, and heat the vessel over a flame. Crude carbolic acid distils over and may be collected in a graduated tube. The process is continued as long as anything passes over. The heat should be increased to dull redness and the contents of the retort occasionally shaken towards the end of the process. On standing, the aqueous portion of the distillate separates from the oily liquid, and the volume of the latter may be read off. A combustion tube of glass or iron, through which a slow current of coal-gas is caused to pass, may be advantageously substituted for the retort. To diminish the loss due to solubility of the carbolic acid, the aqueous layer may be saturated with powdered anhydrous sodium sulphate, when the dissolved carbolic acid will rise to the surface.

When carefully conducted, the foregoing process has yielded fairly satisfactory results, though test experiments have indicated that the proportion of carbolic acid obtained is always below the truth. A better and more accurate process is the following, omitting the treatment with sulphuric acid as unnecessary in the case of siliceous powders.

In the case of powders made with lime, or others in which the carbolic acid exists in combination, the methods of distillation and direct treatment do not give accurate results. For the determination of crude carbolic acid in such powders, the disinfecting value of which is very doubtful, the following method may be employed:—50 grams of the sample should be mixed in a large mortar with 5 c.c. of water. Strong sulphuric acid, previously diluted with an equal bulk of water, is then added very gradually, a few drops only at a time. After each addition the whole is well mixed with the pestle. The addition of the acid, which should extend over some hours, to avoid sensible rise of temperature, is continued until a minute fragment of the well-mixed contents of the mortar shows an acid reaction on moist litmus paper when placed upon it. If the mixture be pasty, sufficient sand is mixed with it to cause it to granulate, and the mortar is then covered up and left for some hours. By proceeding in this way the whole of the lime combines with the sulphuric acid and water to form gypsum, while the car-

bolic acid is liberated. The product is then exhausted with ether or gasoline in a Soxhlet-tube or similar contrivance, and the ethereal solution thus obtained treated with about 20 c.c. of strong soda of 1·20 sp.gr. After agitating, the greater portion of the ether is distilled off and the contents of the flask or retort used transferred to a separator. The ethereal layer which contains the tar oils is evaporated in a tared flask, and, after heating till constant at 100°C., weighed, or, if preferred, measured by some suitable means. It is desirable to shake the soda solution with a fresh quantity of ether and add the ether-washings to the main quantity. Naphthalene, if present, will be removed by the ether. The soda solution is now boiled for a few minutes to remove ether, and acidified in a narrow cylinder with dilute sulphuric acid (1:3). When the liquid has stood some time and is thoroughly cold, the layer of separated phenols is measured. Each cubic centimetre weighs about 1·05 grams. Hence an addition of one-twentieth to the measure gives the correct weight. The results are somewhat below the truth, chiefly owing to the solubility of phenols in aqueous liquids.

J. Muter substitutes alcohol for ether in the foregoing process (Analyst, 12, 191).

The *sulphurous acid* contained in certain disinfecting powders may be determined by stirring 1 grammes of the sample in a mortar with a small quantity of distilled water free from air, and decanting the liquid into a flask containing 50 c.c. of ordinary decinormal solution of iodine and about 250 c.c. of water. The residue in the mortar is repeatedly treated with fresh quantities of water which are transferred to the flask, and the undissolved powder is finally rinsed in. Very dilute hydrochloric acid is now added cautiously until the contents of the flask show a distinctly acid reaction, when the excess of iodine is determined by thiosulphate in the usual way. Each c.c. of decinormal iodine reduced by the sulphite present represents 0·0032 gram of  $\text{SO}_2$ .

**Tribromophenol**  $\text{C}_6\text{H}_3\text{Br}_3\text{OH}$  is one of the newer substances which bid fair to become of some considerable value as antiseptics. According to Dr. Grimm (Ph. J., June 2, 1888), a gauze, containing 2 or 3 p.c. of tribromophenol, when saturated with blood-serum or urine, remains perfectly odourless for fourteen days, whilst a 1 p.c. gauze only begins to smell after five days. 1 p.c. of an ammoniacal solution of tribromophenol added to putrescent blood-serum is said to destroy the bacteria in half an hour, whilst  $\frac{1}{2}$  p.c. solution is effective in one hour. Its presence in a gelatin-cultivation liquid in the proportion of 3 in 1,000 is said to prevent the development of putrefactive bacteria.

When administered internally tribromophenol is taken up by the alkaline secretions of the intestinal canal and eliminated with the urine as tribromophenolsulphonic acid.

**Ortho-phenolsulphonic acid**  $\text{C}_6\text{H}_4 \begin{cases} \text{OH}^{\text{D}} \\ \text{SO}_3\text{H}^{\text{D}} \end{cases}$

This body has been recently introduced as an antiseptic under the names of *aseptol* and *sozolic acid*. It is prepared, mixed with more or less of the para-acid, by mixing equivalent quantities of phenol and strong sulphuric acid in the cold, and removing unacted-on sulphuric

acid by adding barium carbonate. The free sulphonic acid is then obtained by treating the filtered liquid with an equivalent amount of sulphuric acid, and again filtering.

Ortho-phenolsulphonic acid is soluble in water in all proportions, and is also soluble in alcohol or glycerine. It has very little corrosive action, and is practically non-poisonous. It is alleged to have an antiseptic action three times as powerful as that of phenol, while the sodium salt is still more energetic. In its general actions it resembles the para- acid, into which it is converted by heat.

The *aseptol* of commerce is a 33 p.c. aqueous solution of the phenolsulphonic acid.

**Para-phenolsulphonic acid**  $C_6H_4 \begin{cases} OH^{(1)} \\ SO_3H^{(2)} \end{cases}$

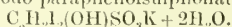
also called sulphophenic or sulphocarbolic acid, is produced commercially by the direct action of concentrated sulphuric acid on phenol. If the acids are diluted beyond a certain point no action takes place.

Para-phenolsulphonic acid is soluble in water and in alcohol, but insoluble in ether and in chloroform. Sulphophenic acid is a decided antiseptic, and its solutions coagulate albumin; but these properties are not shared by the sulphophenates until after addition of acetic acid. The free acid and its salts do not suffer decomposition in aqueous solution even when exposed to the air, and their solutions are not decomposed by boiling. The commercial *sulphocarbols* are salts of para-phenolsulphonic acid.

**Para-phenolsulphonates.** Sulphophenates. The sulphophenates are all soluble in water and mostly soluble in alcohol, especially when hot, but are insoluble in ether. The sodium and calcium salts have been employed in medicine as a means of internally administering carbolic acid. Only distinctly crystalline specimens should be used, and they should have but a very faint odour of phenol.

The presence of unconverted phenol in sulphophenates may be detected by acidulating the solution with dilute sulphuric acid and agitating the liquid with ether or chloroform. The phenol left on spontaneous evaporation of the ether may be detected by its odour and by the yellow colour developed on heating with nitric acid and then neutralising with potash. A faint yellow colour should be neglected, as it may be due to a trace of sulphophenic acid dissolved by the ether.

**Iodo-para-phenolsulphonic acid.** When one molecule of iodine (in the form of a mixture of potassium iodate and iodide) is added gradually to one molecule of potassium para-phenolsulphonate dissolved in excess of dilute hydrochloric acid, iodine at first separates, but is quickly re-absorbed, and after a short time the liquid sets to a dense mass of long thin prisms of potassium diiodo-para-phenolsulphonate,



This salt requires about 50 parts of water for solution, and when heated decomposes without melting at about 270°, with evolution of violet vapours of iodine. The sodium salt (normal) forms a white crystalline powder containing 2 mols.  $H_2O$ , infusible at 200 C. It is odourless, soluble in 13 parts of cold water, and more readily in hot, and is also soluble in alcohol.

*Sozoiodol* is the commercial name given to certain diiodo-phenolsulphonates. 'Easily soluble sozoiodol' is the sodium salt, while the potassium salt forms the 'difficultly soluble' modification (P. J. 3, 18, 538, 621, 1006).

**Thymol**,  $C_{10}H_{13}OH$ . This body, which has the constitution of an isopropyl-methyl-phenol, has marked antiseptic properties, though its cost and insolubility prevent its very extensive application.

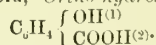
**Naphthols**,  $C_{10}H_7OH$ . Both  $\alpha$ - and  $\beta$ -naphthol possess marked antiseptic properties. According to C. Bouchard (C. R. 105, 702)  $\beta$ -naphthol is a valuable antiseptic for deep wounds of internal administration. 0.33 gram of  $\beta$ -naphthol in 1,000 c.c. of the usual cultivation-liquids prevented the development of eleven species of bacteria, including those of anthrax, chicken cholera, and pneumonia, and a weak cultivation of the typhoid bacillus. It also retarded the development of the bacillus of tuberculosis. It prevented the fermentation of urine, and the production of putrefaction by faecal matter. It is a feeble poison.

According to J. Maximovitch  $\alpha$ -naphthol is more powerfully antiseptic than  $\beta$ -naphthol, and has only one third of the poisonous action. The quantity required to prevent the development of microbes varies from 0.01 to 0.04 p.c., according to the nature of the microbe and the nidus. The only available solvents for naphthol are alcohol and alkaline solutions. The latter materially diminish the antiseptic value owing to the formation of definite compounds, while from the alcoholic solution the naphthol is precipitated by dilution with water. If a solution of soap be employed for diluting the spirit the precipitation is less complete, and, in addition, the viscosity of the liquid facilitates the suspension of the finely divided naphthol. A mixture of camphor and naphthol liquefies at the ordinary temperature, and if naphthol be dissolved in camphorated spirit dilution does not cause complete precipitation of the naphthol, or at any rate the naphthol remains fluid and is more miscible with water.

A preparation, the exact nature of which has not been made public, has been introduced under the name of *hydronaphthol*. It has been alleged that this substance is merely more or less pure  $\beta$ -naphthol, but this is strongly denied, and it is stated to be twelve times as potent as carbolic acid and thirty times as efficient as salicylic acid. It is further said to be non-poisonous, non-corrosive, and harmless, and as a germicide to rank second only to mercuric chloride.

#### AROMATIC ACIDS.

**Salicylic acid**, *Ortho-hydroxybenzoic acid*



This body possesses very marked antiseptic properties, and, owing to its slight taste and its general suitability, it has been used somewhat largely for the preservation of food.

Salicylic acid is soluble with tolerable facility in hot water, but separates for the most part on cooling. Its solubility has been variously stated at from 1 part in 300 to 1 part in 1,000. By the presence of various neutral salts its solu-

bility is increased without its antiseptic value being interfered with. Thus:

Mixed with 1 part potassium nitrate it dissolves in 50 parts of cold water.

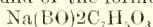
Mixed with  $1\frac{1}{3}$  parts ammonium citrate it dissolves in 60 parts of cold water.

Mixed with 2 parts sodium sulphite it dissolves in 50 parts of cold water.

Mixed with 2 parts sodium phosphate it dissolves in 50 parts of cold water.

Mixed with  $2\frac{1}{2}$  parts sodium phosphate it dissolves in  $12\frac{1}{2}$  parts of cold water.

Salicylic acid is very soluble in solutions of borax, a compound of the formula



being said to be formed. The liquid soon undergoes decomposition. Salicylic acid is soluble in alcohol (1 in  $2\frac{1}{2}$ ); amyl alcohol (1 in 4); ether (1 in 2); chloroform, and benzene (1 in 80). It would appear from recorded experiments that salicylic acid has much greater power as an antiseptic when used for preserving some substances than it has when employed for others. This statement holds good with every antiseptic more or less, but it seems to be particularly the case with salicylic acid.

Bucholtz placed salicylic acid between benzoic and carbolic acids in efficacy, when experimenting with a cultivation-liquid containing sugar, ammonium tartrate, and potassium phosphate. The relative powers which prevented the development of bacteria being: benzoic acid, 1 part in 1,000; salicylic acid, 1 part in 666; carbolic acid, 1 part in 200.

According to the investigations of Koch, salicylic acid, like carbolic acid and thymol, has no antiseptic power if used in solutions made with either alcohol or oil, except when applied to such substances as contain water (*i.e.* flesh &c.), when some of the antiseptic is taken up by the water, and is then rendered active.

Beer and wine can be preserved by the addition of 1 part in 10,000 of salicylic acid. The acid is extensively employed for preserving milk.

*Commercial salicylic acid.* The salicylic acid of commerce is much purer than was formerly the case, when more or less sodium chloride, phenol, cresotic acid, and para- and meta-hydroxybenzoic acids were frequently present. Salicylic acid is stated to have been met with in America adulterated with acid potassium sulphate, gypsum, starch, sugar, &c. Chloride of sodium and other mineral impurities will remain on igniting the sample. Phenol is especially liable to be present in specimens of salicylic acid which have been sublimed. It may be detected by nearly neutralising the solution of the sample with sodium carbonate, and agitating the liquid with ether. On separating and gently evaporating the ethereal layer, the phenol may be recognised by its odour, taste, and chemical reactions.

H. Kolbe tests the purity of commercial salicylic acid by dissolving 0.5 grams of the sample in 5 or 6 c.c. of strong alcohol, pouring the solution into a watch-glass, and allowing it to evaporate spontaneously. The residual salicylic acid forms a ring of beautifully aggregated efflorescent crystals round the edge of the watch-glass. This mass is pure white if the sample of the acid tested be pure and recrystallised, but

yellowish or yellow if the simply precipitated acid be under examination. If the colour be brownish or brown, the acid is unfit for internal use.

The properties of salicylic acid are much modified by the presence of its next homologue, *cresotic acid*,  $\text{C}_6\text{H}_3(\text{CH}_3)_2\text{OH}.\text{COOH}$ . Thus, pure salicylic acid requires about 22 parts of boiling water for solution, while samples containing cresotic acid dissolve in 14 of boiling water, or even a smaller proportion. If to the solution so obtained about one-fifth of alcohol be added, and the liquid allowed to cool, pure salicylic acid will form separate distinct crystals not cohering together, while samples containing cresotic acid form a network or woolly mass of small or indistinct crystals.

*Meta- and para- hydroxybenzoic acids* are said to be occasionally present in commercial salicylic acid. They are stated to have no antiseptic value. They also differ from salicylic acid in not volatilising in a current of steam, and in not yielding the characteristic deep violet colouration with a solution of ferric chloride, a reaction which is common to salicylic acid and the three isomeric cresotic acids.

Many of the metallic salicylates are employed in medicine.

A *basic salicylate of mercury* of the formula  $\text{C}_6\text{H}_4\left\{\begin{array}{l} \text{COOH} \\ \text{COHgOH} \end{array}\right.$  has been recommended for use in place of mercuric chloride in the antiseptic treatment of wounds.

*Salol, Phenyl salicylate*  $\text{C}_6\text{H}_5(\text{OH}).\text{CO}.\text{O}.\text{C}_6\text{H}_5$ . This preparation is now manufactured by heating the product of the action of carbon dioxide on sodium phenate with phosphorus oxychloride or pentachloride, when phenyl salicylate and metaphosphate and chloride of sodium result. Phosgene gas (carbon oxychloride) may be substituted for phosphorus pentachloride (*S. C. I.* 5, 677).

Salol crystallises in rhombic prisms which melt at  $42-43^\circ\text{C}$ . It usually occurs as a white crystalline powder of very faint aromatic odour, but the dilute alcoholic solution has a smell resembling that of winter-green oil, probably owing to the formation of traces of ethyl salicylate. It is almost tasteless, and nearly insoluble in water, but dissolves in alcohol, ether, chloroform, petroleum spirit, and liquefied carbolic acid.

The alcoholic solution of salol is coloured violet by ferric chloride, while bromine gives a precipitate in the form of long needles, consisting of a bromo-derivative,  $\text{C}_6\text{H}_4\text{O}_2\text{Br}$ , crystallising from alcohol in silky needles which melt at  $98.5^\circ\text{C}$ . When boiled with caustic soda, salol is readily saponified, and the solution, when acidulated with hydrochloric acid, gives an odour of phenol and a copious precipitate of salicylic acid, which, after washing with cold water, gives with hot water a solution coloured violet by ferric chloride.

Salol should not redden moistened litmus paper; and when shaken with 50 parts of water should give a filtrate which is not rendered violet on addition of one drop of ferric chloride, nor any immediate change on adding silver nitrate or barium chloride.

Salol is employed in medicine as a substitute for metallic salicylates and winter-green oil.



Being insoluble, it passes unchanged through the stomach, but in the duodenum is decomposed into phenol and salicylic acid, and these products can be detected in the urine, which is usually very dark in colour, as after the ingestion of phenol, of which salol contains 38 p.c. As an antipyretic, antiseptic, and antirheumatic, salol possesses properties of value. When applied externally it has no corrosive action, and its lower melting-point gives it some advantages over salicylic acid.

According to Löwenthal (C. R. 107, 1169), salol will kill cholera bacilli already developed in a paste containing pancreatic juice, and its addition to a paste before the sowing of the bacilli will render the paste sterile.

*Cresyl salicylates* are obtained by processes analogous to that used for the preparation of salol. They resemble salol and have a similar antiseptic value, but have not so strong an odour. The salicylate from orthocresol melts at 35°C., that from metacresol at 71°C., and that from paracresol at 39°C. In the system they are split into salicylic acid and the cresols from which they are derived. In the case of the compound from paracresol, the cresol is eliminated partly as a cresyl-sulphuric acid.

A body analogous to salol may be obtained by substituting resorcinol for phenol.

*Naphthyl salicylate*  $C_{10}H_7(OH)CO.O.C_{10}H_7$ , a body analogous to salol, has been introduced into commerce under the name of 'betol.' It forms small, lustrous crystals, melting at 203°, almost devoid of taste, and insoluble in water, but soluble in alcohol and fatty oils.

**Carbophenanthrolic acid**, a body prepared by acting on naphthol with carbon dioxide in presence of sodium, is said to have powerful antiseptic properties, though somewhat poisonous.

**Benzoic acid**, *Phenylformic acid*  $C_6H_5.CO.OH$ . R. G. Eccles recommends benzoic acid as being less objectionable than most of the ordinary antiseptics when used for most internal purposes, or applied to a delicate membrane or delicate portion of the body (such as the eye, in collyria), &c.

He considers that it can be used with advantage to preserve alkaloidal solutions, such as are now becoming more and more used in ophthalmic surgery, and states that when such solutions are applied to the eyes, the benzoic acid employed does not produce the least irritation.

It possesses about 60 times the antiseptic value of boric acid. According to some observers its antiseptic value is superior, and, according to others, inferior, to salicylic acid.

It does not impair the flavour of fruit juices. It is excreted as hippuric acid, a normal constituent of urine.

**Sodium benzenesulphinate** is a compound obtained by dissolving benzoic acid in a concentrated solution of sodium sulphite. It is very soluble in water at the ordinary temperature, and the solution has been recommended as an antiseptic dressing for wounds. It is said to be more efficient than phenol, and to rank with mercuric salts and iodoform, without having the poisonous characters of the former, or the disagreeable odour of the latter.

**Cinnyl alcohol** possesses valuable antiseptic properties, being as powerful in this respect as

thymol. A saturated aqueous solution forms a convenient dressing for ulcerated surfaces.

#### BASIC DISINFECTANTS.

Certain organic bases have antiseptic properties of a very high order. Thus the value of creosote oils for preserving timber is probably materially increased by the presence of *acridine*,  $C_{13}H_9N$ . *Pyridine* and its analogues have also antiseptic properties, and their employment has formed the subject of several patents.

**Hydroxylamine** and **phenylhydrazine** have also been found to have marked antiseptic properties, and the same is probably true of many similar bodies.

**Trimethylamine** does not appear to be a powerful antiseptic; but, according to Wolheim, on adding milk of lime to herring-brine a 'soluble gaseous reagent' is produced which is highly inimical to bacterial life. It is stated that sewage treated with a small proportion of lime and herring-brine is sterilised so perfectly that neither the precipitate nor liquid shows any further tendency to putrefy.

#### ESSENTIAL OILS.

Many of the essential oils possess well-marked disinfectant properties, a character which in some cases is probably associated with the formation of hydrogen peroxide. This property has been utilised by C. T. Kingzett in the preparation of the disinfectant commercially known as *Sanitas* by the action of air and water on oil of *turpentine*. The value of *eucalyptus* oil is well known.

W. Leonard Braddon (Lancet, March 24, 1888, 179), has directed attention to the valuable antiseptic properties of oil of *peppermint*, and points out that Koch found that one part of this oil in 300,000 arrested the development of the spores of the charbon bacillus, and that the vapour speedily killed both spores and bacilli. Braddon considers oil of peppermint one of the strongest and most reliable of antiseptic agents, and has found marked good effects from its use in diphtheria and the early stages of phthisis.

A. H. A.

**DISTILLATION.** The object of distillation is the separation of a volatile liquid from a non-volatile substance, such as pure water from sea water, or more commonly the separation of two or more liquids of different volatility.

The apparatus required consists essentially of four parts; a still or boiler, A, fig. 1, in which

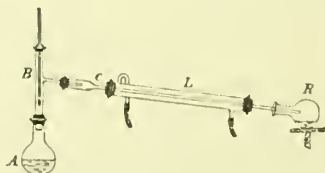


FIG. 1.

the liquid is boiled; a upright tube or head, B; a condensing tube, C, sloping downwards and cooled by suitable means—a Liebig's condenser, L, through which a current of water is passed, being generally employed in the laboratory;

lastly, a receiver, R, to collect the distilled liquid. The form of apparatus shown in fig. 2 is convenient for many purposes; the still, the head, and the condensing tube are sealed together in one piece.

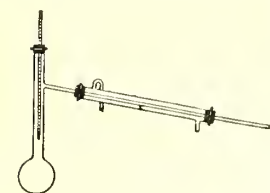


FIG. 2.

The still is usually heated by the flame of a Bunsen burner, but for very volatile and inflammable liquids a water bath should be used; the Liebig's condenser is unnecessary for liquids which boil above  $160^{\circ}$  or  $170^{\circ}$  if the condensing tube is fairly long.

If the temperature at which the liquid boils is to be ascertained with accuracy, and this is generally the case in fractional distillation, especially in the final purification of a liquid, the following points should be attended to.

1. The thermometer should be carefully calibrated, and it would be a great advantage if all thermometers were compared with an air thermometer, for different kinds of glass expand very differently when heated, and therefore two thermometers, constructed of different varieties of glass, will give different readings, especially at high temperatures.

2. The zero point of the thermometer should be redetermined from time to time. It is a good plan to heat the thermometer for several hours to about  $300^{\circ}$  or  $360^{\circ}$  before calibrating it; the subsequent changes of zero point, which otherwise might be considerable at high temperatures, are thereby greatly reduced. (Crafts, C. R. 95, 910; also several earlier papers.) Thermometers treated in this manner may now be purchased.

3. For high temperatures the thermometers should contain nitrogen to prevent volatilisation of mercury in the heated stem; if the thermometer is provided with a small bulb at the top, rise of pressure owing to compression of the gas in the thermometer is avoided.

4. The thermometer should, if possible, be so placed in the apparatus that not only the bulb but also the column of mercury in the stem is surrounded by the vapour of the boiling liquid; otherwise the following correction, which at the best is somewhat uncertain, must be applied:—

$N$  = length of column of mercury in scale degrees not heated by vapour.

$T$  = temperature of vapour (the approximate temperature directly read on the thermometer is usually sufficiently accurate).

$t$  = mean temperature of column of mercury not heated by vapour. This temperature may be approximately ascertained by attaching a small thermometer to the other by means of thin india-rubber bands or wire, with its bulb at about the middle of the unheated column.

Correction—add  $0.000143 (T-t)N$ .

The co-efficient  $0.00016$  is usually employed, but Holtzmann pointed out that this is too high, and adopted the number  $0.000135$ ; Thorpe, however (C. J. 1880, 159), has shown that the co-efficient  $0.000143$  gives the best results.<sup>1</sup> The

<sup>1</sup> Rimbach (B. 22, 3072) has constructed tables of corrections by interpolation from experimental data up to  $220^{\circ}$  for two kinds of thermometers graduated in degrees, and up to  $100^{\circ}$  for thermometers graduated in tenths of a

following table for the correction of thermometer readings is taken from Thorpe's paper:—

$T-t$	$N$															
	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160
10	0.01	0.03	0.04	0.06	0.07	0.09	0.10	0.11	0.13	0.14	0.16	0.17	0.19	0.20	0.21	0.22
20	0.02	0.06	0.09	0.11	0.14	0.17	0.20	0.22	0.26	0.29	0.31	0.34	0.37	0.40	0.43	0.46
30	0.04	0.09	0.13	0.17	0.21	0.26	0.30	0.34	0.39	0.43	0.47	0.51	0.56	0.60	0.64	0.68
40	0.05	0.11	0.17	0.23	0.28	0.34	0.40	0.47	0.52	0.57	0.63	0.69	0.74	0.80	0.86	0.91
50	0.07	0.14	0.21	0.29	0.36	0.43	0.50	0.60	0.67	0.71	0.79	0.86	0.93	1.00	1.07	1.14
60	0.08	0.17	0.25	0.35	0.43	0.51	0.60	0.70	0.77	0.86	0.94	1.03	1.12	1.20	1.29	1.37
70	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00	1.10	1.20	1.30	1.40	1.50	1.60
80	0.11	0.23	0.34	0.45	0.57	0.68	0.80	0.91	1.03	1.14	1.26	1.37	1.49	1.60	1.72	1.83
90	0.13	0.26	0.39	0.51	0.64	0.77	0.90	1.03	1.16	1.30	1.42	1.54	1.66	1.80	1.93	2.05
100	0.14	0.29	0.43	0.57	0.71	0.85	1.00	1.14	1.29	1.43	1.58	1.71	1.84	2.00	2.15	2.29
110	0.16	0.31	0.47	0.63	0.78	0.94	1.10	1.26	1.42	1.58	1.73	1.89	2.04	2.20	2.36	2.51
120	0.17	0.34	0.51	0.69	0.86	1.03	1.20	1.37	1.54	1.71	1.89	2.06	2.23	2.40	2.57	2.74
130	0.19	0.37	0.56	0.74	0.93	1.12	1.30	1.49	1.66	1.84	2.02	2.20	2.38	2.56	2.74	2.92
140	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.80	2.00	2.20	2.40	2.60	2.80	3.00	3.20
150	0.21	0.43	0.64	0.86	1.07	1.29	1.51	1.72	1.93	2.15	2.36	2.57	2.78	3.00	3.21	3.43
160	0.22	0.46	0.68	0.91	1.14	1.36	1.58	1.80	2.01	2.23	2.45	2.67	2.88	3.10	3.32	3.54
170	0.24	0.49	0.73	0.97	1.22	1.46	1.70	1.94	2.17	2.41	2.65	2.89	3.13	3.37	3.61	3.85
180	0.26	0.51	0.77	1.03	1.29	1.54	1.80	2.05	2.31	2.56	2.81	3.06	3.31	3.56	3.81	4.06
190	0.27	0.54	0.82	1.09	1.36	1.63	1.90	2.17	2.44	2.71	2.98	3.25	3.52	3.79	4.06	4.33
200	0.29	0.57	0.86	1.14	1.43	1.72	2.00	2.28	2.56	2.84	3.12	3.40	3.68	3.96	4.24	4.52

5. When the amount of liquid in the bulb is very small the vapour is liable to be superheated

degree. All these thermometers were constructed of Jena glass, and from the results it would appear that the form of the thermometer, and doubtless also the nature of the glass, have a notable influence on the magnitude of the correction.

by the flame, and unless the bulb of the thermometer is thoroughly moistened with condensed liquid, too high a temperature will be registered. If a very little cotton-wool or, for temperatures above  $230^{\circ}\text{C}$ ., a little fibrous asbestos be wrapped round the bulb of the thermometer, it remains thoroughly moist, and with a pure liquid the thermometer registers a perfectly constant temperature until the last trace of liquid in the bulb has disappeared (Ramsay and Young, C. J. 1885, 42).

6. The barometer should always be read, and corrected to  $0^{\circ}\text{C}$ ., for the boiling-point of a liquid varies greatly with the pressure. It is impossible to give any accurate and generally applicable formula for correcting the observed boiling-point to that under normal pressure (760 mm.), but the following may be taken as fairly approximate:

$$\theta = (p - 760) \cdot \frac{273 + t}{8200} \text{ or } \theta = (p - 760) \cdot \frac{273 + t}{10000}$$

where  $\theta$  is the correction in degrees centigrade,  $t$  is the observed boiling-point, and  $p$  is the barometric pressure.

The first correction is applicable to the majority of liquids, the second to water and the lower alcohols (Ramsay and Young, P. M. 1885, 515). For a more accurate method of correction *v. Crafts* (B. 20, 709). It is probable that the wide differences observed by different chemists in the boiling-point of many liquids not very difficult to obtain in a fair state of purity may be accounted for by the neglect of some of the precautions described.

The various parts of the simple apparatus, figs. 1 and 2, may require modification under certain circumstances.

*The still.* For larger quantities of liquid a tin or copper vessel is preferable to glass.

*The head.* The modifications of this part of the apparatus will be considered under fractional distillation.

*The condenser.* For very volatile liquids the condensing tube must be cooled by ice or a freezing mixture (pounded ice and salt or ice and concentrated hydrochloric acid, &c.). In

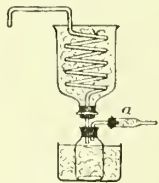


FIG. 3.

this case a spiral or 'worm' tube should be used (fig. 3). Condensation of moisture in the receiver is prevented by the drying tube *a*.

*The receiver.* If a liquid boils at a very high temperature, or if it suffers decomposition at the ordinary boiling-point, it may be necessary to distil it under reduced pressure. For cases of simple distillation the apparatus shown in fig. 4 may be employed, but if the distillate is to be collected in separate portions, as in fractional distillation, the removal of the receiver would necessitate the admission of air into the apparatus and a fresh exhaustion after each change. This inconvenience may be obviated by the em-

ployment of stopcocks arranged in such a manner that air may be admitted into the receiver and a fresh one put in its place while the distillation

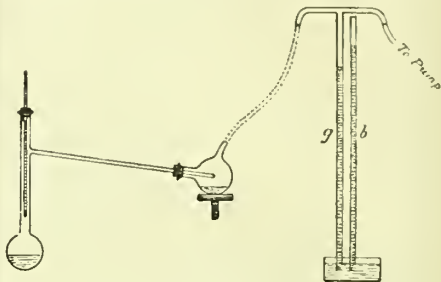


FIG. 4.

bulb remains exhausted. (Thörner, B. 9, 1868; F. D. Brown, C. J. 1879, 554; L. T. Thorne, B. 16, 1327 (fig. 5); Lothar Meyer, B. 20, 1834.)

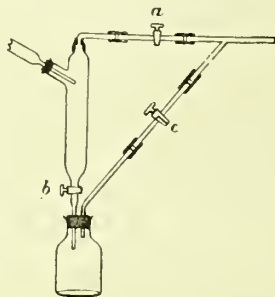


FIG. 5.

Or again a series of receivers on a revolving stand placed under an exhausted bell-jar may be employed. (Gorhoff and Kessler, B. 18, 1363; Brühl, B. 21, 3339 (fig. 6).)

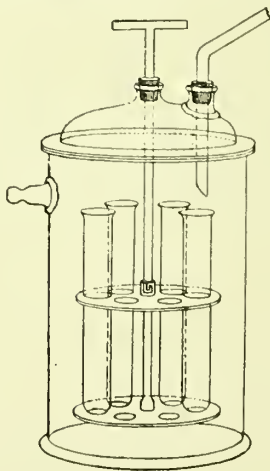


FIG. 6.

Many liquids absorb moisture from the air or are acted upon by oxygen, and in these cases special precautions must be taken, the moist air



in the apparatus being expelled and replaced by dry air, carbon dioxide, nitrogen, or hydrogen; the receivers must also be protected by drying tubes. For example, *v. Thorpe*, C. J. 1885, 120.

**Theory of distillation.** Investigations of the vapour pressures of liquids have thrown much light on the subject of distillation. If a pure liquid be confined in the space above the mercury in a barometer tube, it will evaporate until the pressure of its vapour—measured directly by the depression of the mercury column—has reached a definite amount, which, for a given substance, and if liquid be still present, depends solely on the temperature. From the readings of pressure at various temperatures we may construct a curve to illustrate the relations of temperature to pressure for a given substance, but this curve has a two-fold meaning, for it represents not only the vapour pressures (vapour tensions) at definite temperatures, but also the boiling-points of the liquid under definite pressures. Thus the vapour pressure of pure water at 100°C. is 760 mm. of mercury at 0° and under a pressure of 760 mm. water boils at 100°. Again, the vapour pressure of water at 0° is 4·6 mm., and if the pressure in a distillation bulb containing water be reduced to 4·6 mm. the water will boil at 0°. The truth of this general statement was conclusively proved by *Regnault* (*Mém. de l'Académie*, vols. 21 and 26).

*Regnault* has also investigated the behaviour of mixed or heterogeneous liquids, which he divides into three classes:—1. Liquids which are quite or almost insoluble in each other; 2. Liquids which are miscible only within certain limits; 3. Liquids which mix in all proportions. *Regnault* employed both the statical and dynamical methods of investigation, that is to say, he determined on the one hand the vapour pressures of the heterogeneous liquids at various temperatures in the barometer tube, and on the other hand the boiling-points of the liquids under various pressures.

I. The first class of heterogeneous liquids gives the simplest results, for the vapour pressure at any temperature is—approximately at any rate—the sum of the vapour pressures of the constituents at the same temperature; in other words, the liquids evaporate independently of each other (*v. also Magnus*, P. 38, 488). It is obvious, however, that we must not have one liquid covered by a long column of the other, especially if the heavier liquid is also the less volatile. In this observation of *Regnault's* lies the explanation of the fact that liquids which boil at a much higher temperature than water and are insoluble in it, pass over with the steam when the two substances are distilled together. This process of distillation with steam is very frequently made use of in order to separate high boiling liquids such as aniline from non-volatile impurities; it is especially useful when the liquid is liable to decompose at its ordinary boiling-point.

If this generalisation is rigorously correct, and if we know the vapour pressures of the two non-miscible liquids, we can calculate the temperature at which the heterogeneous liquid will boil—so long as the relative quantity of either liquid is not too small—and also the relative

weights or volumes of the two liquids in the distillate.

The following example will illustrate the method of calculation. The substances are water and chlorobenzene, the vapour pressures of which are accurately known.

Temperature	Vapour pressure		
	Chlorobenzene	Water	Total
90°	208·35	525·45	733·8
91°	215·8	545·8	761·6
92°	223·45	566·75	790·2

Under a pressure of 761·6 mm. the heterogeneous liquid should boil at 91·0°.

In a litre of the vapour at 91° and 761·6 mm. we shall have, according to Dalton's law of partial pressures, 1 litre of chlorobenzene at 91° and 215·8 mm. and 1 litre of steam at 91° and 545·8 mm. Now the vapour density of chlorobenzene is 56·2 and of water 9; therefore the weights of chlorobenzene and water in a litre of the mixed vapour will be—

$$\text{Chlorobenzene } \frac{0\cdot0896 \times 56\cdot2 + 273 \times 215\cdot8}{(273 + 91) \times 760}$$

$$\text{Water } \frac{0\cdot0896 \times 9 \times 273 \times 545\cdot8}{(273 + 91) \times 760}$$

or the relative weights will be  $\frac{56\cdot2 \times 215\cdot8}{9 \times 545\cdot8}$ ; or

generally, if *d* and *D* be the vapour densities of the two liquids and *p* and *P* their vapour pressures at the calculated boiling-point, the ratio of the weights in the vapour and therefore

in the distillate will be  $\frac{w}{W} = \frac{dp}{DP}$  (*v. Nau-*

*mann*, B. 10, 1421, 1819, 2015, 2099, and *Brown*, C. J. 1879, 550). That these laws are in accordance with the facts may be seen from the following experiment. Eighty grams of water and 110 grams of chlorobenzene were distilled until about 3 grams of chlorobenzene and nearly 40 of water remained in the flask. Bar. pressure 740·2 mm. Boiling-point calculated 90·25; observed 90·25 to 90·35. Percentage by weight of chlorobenzene in distillate:—calculated 71·2; observed 71·6. The distillate was collected in five portions, each of which had practically the same composition. On continuing the distillation the temperature rose rapidly when the chlorobenzene had nearly disappeared.

The following laws hold good for the distillation together of two (or more) insoluble liquids:—

1. The boiling-point is lower than that of either component, and may be calculated if the vapour pressures of the components are known; it remains constant until nearly the whole of either of the liquids has been removed.

2. The composition of the distillate remains constant until the quantity of either component has become very small; it may be calculated from the equation  $\frac{w}{W} = \frac{dp}{DP}$ .

Many experiments might be cited in support of these laws, and though the vapour pressures have in many cases not been determined, so that

the evidence is frequently incomplete, still, taken as a whole, it seems conclusive (Pierre and Puchot, A. Ch. 163, 293; Hecht, *ibid.* 209, 321; Lazarus, B. 18, 577; Rasinski, J. pr. 31, 428).

II. We come now to Regnault's second class of binary liquids, those which are only partially miscible. Not very much is accurately known about such heterogeneous liquids, and it is doubtful whether any definite laws can be enunciated further than that the vapour pressure is greater than that of either liquid alone, but is less than the sum of the two, and that the boiling-point under any pressure is lower than that of the more volatile component. The boiling-point cannot, however, be calculated from the vapour pressures of the components. In the case of aniline and water, which are but slightly soluble in each other, the lowest temperature observed was 0.85° higher than that calculated, and with excess of aniline it rose 1° while there was still a good deal of water present. The composition of various fractions was nearly constant, but the percentage of aniline (correcting for approximate solubility) was more than 3 p.c. lower than that calculated (*v.* Konowalow, Wied. Ann. 14, 219; Pierre and Puchot, *l.c.*).

III. Regnault's third class of binary liquids includes those which are miscible in all proportions, but the behaviour of such mixtures varies so greatly that it is convenient to subdivide them into three groups.

a. When the liquids are mixed in certain proportions, the vapour pressure is higher and the boiling-point is lower than that of either component alone; for each pair of substances that mixture which exerts the greatest vapour pressure, and which therefore has the lowest boiling-point, boils at a constant temperature, and it is impossible to separate the components by any system of fractional distillation.

b. The vapour pressure and the boiling-point of the mixture always lie between those of the components, whatever the proportions; there is no mixture of constant boiling-point, but the temperature rises continuously during distillation. The components may be separated by fractional distillation.

c. With mixtures of a certain composition the vapour pressure is lower and the boiling-point higher than that of either component. A mixture of constant boiling-point may be obtained, which cannot be altered in composition by fractional distillation; it is this mixture which has the maximum boiling-point and the minimum vapour pressure.

An explanation of the very varied behaviour of different pairs of liquids when heated together may probably be found in the following considerations. When two liquids A and B are brought in contact three factors must be taken into account (1) the attraction of the molecules of A for each other; (2) the attraction of the molecules of B for each other; (3) the attraction, whether physical or chemical, of the molecules of A for those of B. The relative magnitude of these attractions appears to be manifested in various ways, for instance, by the miscibility of the liquids; by the heat evolved or absorbed on mixing; by the change of volume on mixing; by the effect on the vapour pressure or boiling-point.

The simplest case is that in which the attraction of the molecules of A for each other and of those of B for each other is incomparably greater than the attraction of the molecules of A for those of B. In this case the liquids do not mix at all; there is obviously no heat evolution or change of volume; and the vapour pressure is the sum of those of the components. The boiling-point and the composition of the vapour or distillate may be calculated by the method given.

As the relative value of the attraction of the unlike molecules increases, the liquids taken become more and more miscible until we get liquids which mix in all proportions. Again, taking the same order, we have at first in all probability absorption of heat on mixing, the amount of heat absorbed gradually diminishing and finally changing to an increasing heat evolution. So also with the change of volume, we have expansion at first, but this diminishes, and we finally observe a contraction on mixing the liquids. Lastly, the vapour pressure becomes relatively smaller and smaller than the sum of those of the components and the boiling-point higher than that calculated on the basis of complete insolubility, until, as in the case of formic acid and water, we find that the vapour pressure—for certain proportions—is less and the boiling point is higher than that of either component.

In connection with this part of the subject a striking observation by Hecht (A. 209, 321) may be mentioned. On distilling a mixture of acetic acid (b.p. 119°), butyric acid (b.p. 163°), and cœnanthylic acid (b.p. 223°) with excess of water, the cœnanthylic acid came over first, then the butyric acid, and lastly the acetic acid. Hecht points out that cœnanthylic acid is insoluble in water; butyric acid is soluble in all proportions, but without apparent heat evolution, and acetic acid evolves heat when mixed with much water.

But the effects produced by increasing attraction of unlike molecules probably do not always proceed as it were *pari passu*. Thus while it is generally the case that the vapour pressure of a mixture of two liquids which dissolve in each other in all proportions lies between those of the components, yet there is a considerable number of cases known in which the vapour pressure is greater than that of the more volatile component.

It is well known that the solubility in water of many homologous series of fatty compounds, alcohols, aldehydes, acids, &c., diminishes with rise of molecular weight, and, as far as experiments on the subject have been made, it appears that the contraction and the heat evolution on admixture with water also diminish. The vapour pressures of various mixtures of the lower fatty alcohols and acids with water have been carefully studied by Konowalow (Wied. Ann. 14, 34) and the results are very clearly exhibited by means of curves. Konowalow shows that the vapour pressures of mixtures of methyl alcohol and water always lie between those of the components, and it is well known that this is also the case with the boiling-points. This is also the case with mixtures of ethyl alcohol and water, in nearly all proportions, but according to

Le Bel (C. R. 88, 912) a mixture containing about 97 p.c. of alcohol boils at a constant temperature; but with propyl alcohol addition of water raises the vapour pressure and lowers the boiling-point, and a mixture of about 28 p.c. of water and 72 p.c. of propyl alcohol boils with perfect constancy at a temperature nearly  $10^{\circ}$  below the boiling-point of the more volatile component, propyl alcohol. The behaviour of isobutyl alcohol and water approximates very closely to that of two non-miscible liquids. Again, with the acids, addition of water lowers the vapour pressure of formic acid, the minimum being reached with from 20 to 30 p.c. of water, while Roscoe has shown that a mixture containing 77.5 p.c. of formic acid boils constantly at  $107^{\circ}$ , the boiling of formic acid being  $101.1^{\circ}$ . Acetic acid shows nothing of the kind, the vapour pressure and boiling-point lying always between those of the components. The mixtures of the higher acids with water behave more and more like non-miscible liquids.

In accordance with these results it is found practicable to effect a fairly complete separation of methyl or ethyl alcohol or acetic acid from water by distillation, but it is quite impossible to do this with propyl alcohol or formic acid. In the case of propyl alcohol the first portions of the distillate consist of the constant boiling mixture, the last portions, however, consisting of either pure water or propyl alcohol, according to the relative quantities in the original mixture; while with formic acid pure or fairly pure water or acid comes over first and the temperature gradually rises until the constant boiling mixture begins to distil, after which it remains constant until the end of the distillation.

As regards the composition of the distillates from mixtures of class III., it has been stated by Wanklyn (A. 128, 328) and also by Berthelot (*ibid.* p. 321) that the law which has been shown to apply to non-miscible liquids is true for all mixtures, and confirmatory results have been obtained by Thorpe (C. J. 1879, 544) in the case of a mixture of equal volumes of carbon tetrachloride and methyl alcohol, but it is to be noticed that the mixtures examined belong to class IIIa., the boiling-point in each case being (for certain proportions) lower than that of either component. A very laborious series of experiments has been made by F. D. Brown (C. J. 1879, 550; 1880, 49, 304; 1881, 517) with a view to determining the relation between the composition of the distillates from mixtures of varying composition and the boiling-points of those mixtures. Brown finds that Wanklyn's law does not hold for ordinary mixtures, the boiling-points of which rise continuously during distillation. Calling the relative weights of the two liquids in the mixture in the still  $W_1$  and  $W_2$ , the relative weights in the distillate  $x_1$  and  $x_2$  and the vapour pressures of the pure substances at the boiling-point of the mixture  $P_1$  and  $P_2$ , the following relation was found to be not very far from correct

$$\frac{x_1}{x_2} = \frac{W_1}{W_2} \cdot \frac{P_1}{P_2},$$

but by substituting a constant for the ratio  $\frac{P_1}{P_2}$  closer agreement was obtained, thus  $\frac{x_1}{x_2} = \frac{W_1}{W_2} \cdot C$ .

The cases of fractional distillation which we have most commonly to deal with are those in which the separation of two or more liquids which are miscible in all proportions is to be effected, and it generally happens that the boiling-point of the mixture rises continuously during distillation. The ease with which the separation of any two such substances is effected by distillation depends chiefly on two points: (1) The divergence of the boiling-points; (2) the influence of successive additions of one component on the boiling-point (or vapour pressure) of the other. The second point has been carefully studied by Konowalow (*l.c.*), and the curves for mixtures of ethyl alcohol and of acetic acid with water are very instructive. In the case of alcohol at  $79.65^{\circ}$  the curve shows that the addition of small quantities of alcohol to water raises the vapour pressure of the mixture very rapidly, but the addition of small quantities of water to pure alcohol has very little effect on the vapour pressure. With acetic acid the results are precisely the reverse. An examination of the curves shows that the effect of admixture on the boiling-points must be very similar to that on the vapour pressures, and the results obtained in practice are in perfect accordance with those deducible from Konowalow's curves. It is well known that when a mixture of alcohol and water is distilled the first portions of the distillate are rich in alcohol, but always contain some water, and it is impossible to obtain perfectly anhydrous alcohol by fractional distillation (Le Bel, *l.c.*); but it is quite easy to obtain pure water from a mixture of that substance with a little alcohol. Again, pure acetic acid may be obtained by distillation of its concentrated aqueous solution, but pure water cannot be separated without considerable difficulty from a dilute solution of acetic acid.

It is clear that the preparation of even approximately anhydrous alcohol from the dilute aqueous solution or from the fermented worts from which it is obtained on the large scale would be a very slow process if the ordinary methods of distillation were adopted, and various contrivances have been devised to increase the efficiency of the process in this and in other cases.

As a matter of fact most of the improvements in the methods of distillation were employed in commerce before they were introduced into the laboratory, but it may be more convenient to describe those used in the laboratory first.

The modified forms of apparatus may be divided into three classes. In the first, the still-head or vertical tube through which the vapour passes from the still to the condenser is considerably elongated or is expanded into a series of bulbs, in order that the vapour may be partially condensed and some of the less volatile constituents removed before it reaches the condenser. In the second class the still-head is further modified in such a manner that the vapour has to force its way through several short columns of the condensed liquid; this process is termed 'dephlegmation,' but the term is sometimes applied to processes coming under class I. In the third class the still-head is not greatly modified in form, but is elongated, and is kept at a constant temperature as near as possible to that of the lowest boiling constituent of the mixture.



The employment of an elongated still-head provided with a series of bulbs (fig. 7) was first suggested by Wurtz; it gives better results than the plain distillation bulb, but is generally inferior to the modified still-heads coming under classes II. and III.

The 'dephlegmator' has long been employed in the arts; its adoption in the laboratory seems

(C. J. 1880, 57); v. also Warren de la Rue (Fr. 4, 243). An apparatus devised by Winssinger (B. 16, 2640) cannot very well be classified with the others. The vapours in the vertical still-head are partially cooled by a regulated current of water flowing through a double tube placed in the head and reaching as far as the distillation flask; they then pass by a side tube, which is extended vertically to admit a thermometer, into the condenser (v. also Rempel, C. Z. 10, 371).

Experiments to test the relative efficiency of these various forms of apparatus have been made by Kreis, A. 224, 259; Claudon, Bl. 42, 613; Brown, C. J. 1880, 49.

Kreis finds that for substances boiling at moderate temperatures the dephlegmators of Linnemann and of Hempel give the best results, and he recommends the latter on account of its simplicity. With high boiling substances the apparatus of Wurtz (scaled to the distillation flask) was most satisfactory. Kreis did not try any modification of Warren's apparatus. Claudon prefers the apparatus of Le Bel and Henninger to that of Winssinger.

Brown shows that the dephlegmator is much superior to a plain cooling tube of the same dimensions, but that a still-head of constant temperature gives still better results (v. also Lunge, C. Z. 50, 896; D. P. J. 254, 70).

When two or more liquids are to be separated by fractional distillation, the mixture is placed in a distillation flask, preferably provided with a Wurtz's still-head or dephlegmator, and boiled, the temperature being read as soon as the vapour reaches the condenser. The distillation is allowed to proceed until the temperature has risen through a certain interval, depending on the nature of the mixture, when the receiver is removed and a fresh one substituted. After a further rise of temperature to the same or a convenient extent the receiver is again changed, and this process is continued until the whole of the liquid has passed over. The apparatus is then cleaned, and the fractions obtained from the first operation are separately distilled, but the procedure followed by different chemists is not always identical. Probably the best, and undoubtedly the most systematic, plan is to begin with the first fraction and to proceed with its distillation, collecting the new distillate again in the first receiver, until the temperature has risen to the point at which the first change of receiver was made. The distillate in the second receiver is then to be added to the residue in the flask and the distillation proceeded with, the first receiver being left in position until the temperature has again reached the point at which the first change was made. The second receiver is then to be substituted for the first, and the distillation continued until the temperature has risen through the second interval. The third fraction is then to be placed in the flask and the process repeated as before.

An example, taken from Kreis's paper, may make the process clearer. The mixture consisted of 25 grams of benzene and 25 grams of toluene, and the intervals of temperature were in all cases 3°. The progress of the separation is clearly

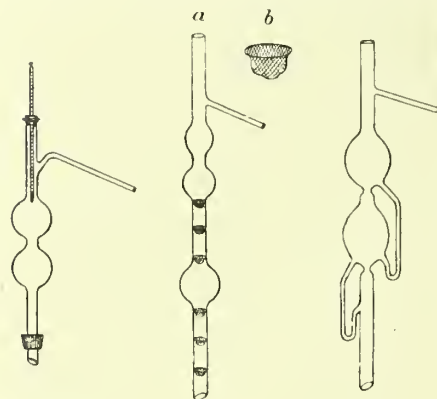


FIG. 7.

FIG. 8.

FIG. 9.

to have been first proposed by Linnemann in 1871 (A. 160, 195). The form of apparatus devised by Linnemann is shown in fig. 8. Various improvements have been suggested by Le Bel and Henninger (fig. 9) (B. 7, 1084) and by Glinsky (fig. 10) (A. Ch. 175, 381). The employment of an upright tube constricted near the bottom and containing glass beads was recom-

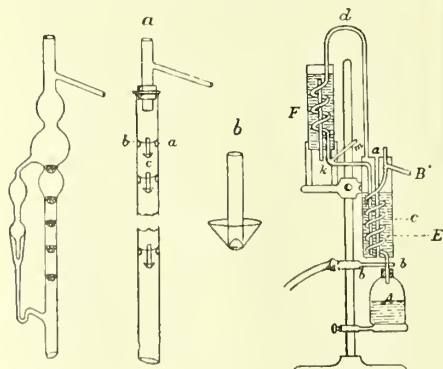


FIG. 10.

FIG. 11.

FIG. 12.

mended by Hempel (Fr. 20, 502). Lastly, an easily constructed form of dephlegmator (fig. 11) has been described by F. D. Brown (C. J. 1880, 49).

The employment of an elongated spiral still-head kept at a constant temperature was first recommended by Warren (A. Suppl. 4, 51). The spiral still-head was heated in an air-bath. A modification of this apparatus, devised with a view to the better control of the temperature of the still-head, is described by F. D. Brown (fig. 12)

shown by the table in which the results of six complete fractionations are given :

Temperature	Vo'lume of distillate in cubic centimetres					
	I.	II.	III.	IV.	V.	VI.
81-84 . . .	1.0	9.0	17.0	19.5	21.5	22.0
84-87 . . .	10.0	9.5	7.0	5.5	4.5	3.5
87-90 . . .	14.5	8.5	4.5	4.0	3.0	2.0
90-93 . . .	8.0	5.0	3.5	2.5	1.5	1.5
93-96 . . .	6.0	3.5	3.0	2.0	2.0	1.0
96-99 . . .	5.5	3.5	2.0	2.5	1.5	1.0
99-102 . . .	2.5	2.5	2.5	1.5	1.5	1.0
102-105 . . .	3.5	4.0	2.5	2.0	1.5	1.0
105-108 . . .	3.5	3.5	2.5	1.5	1.5	1.5
108-111 . . .	3.5	7.5	10.5	13.0	14.5	16.0

As the fractionation of a mixture of liquids proceeds it is found that the distillates for certain intervals of temperature accumulate greatly, while those for others become very small; it is then generally advisable to narrow the intervals of temperature for the larger portions and to extend those for the smaller, and as the purity of those large fractions increases the corresponding temperature intervals may be made smaller and smaller, until finally constant boiling fractions are obtained (*v. Mendeleeff*, Journ. Russ. Phys. Chem. Soc. Protok. 1883, 189). For substances insoluble in water fractional distillation with steam sometimes gives good results (*Lazarus*, B. 18, 577).

As many of the stills used in the arts are described under the headings 'Alcohol,' 'Benzene,' 'Paraffin,' &c., it will be unnecessary here to give a minute description of all of them, but an account of the principles underlying the different methods will not be out of place.

The still is usually made of copper or some other metal, and may be heated by the free flame of a furnace or by steam. Fig. 13 shows an

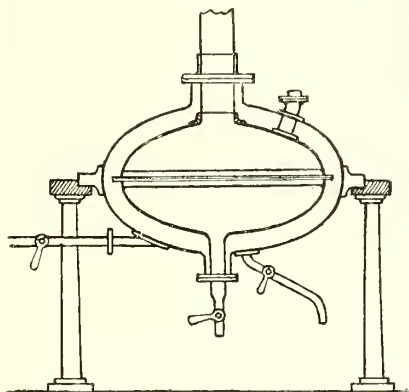


FIG. 13.

arrangement for heating a still with steam, which may be above the atmospheric pressure.

When only a rough separation of the constituents of a complex mixture is required, as in the preliminary distillation of coal tar, dephlegmators or rectifiers are not employed, but the vapours pass directly from the still to the condenser.

For the better separation of the components of a mixture, modified still-heads are employed.

A simple apparatus, devised by Mansfeld for the distillation of tar oils, is shown in fig. 14; the vapours are partially condensed in the still-head A,

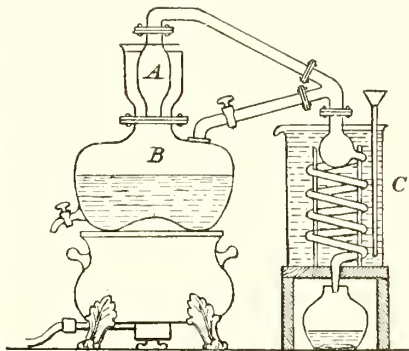


FIG. 14.

which is cooled by water, and the condensed liquid flows back into the still B, the purified vapour passing on to the condenser C.

A more perfect separation is effected by Coupiér's apparatus (fig. 15). In addition to the

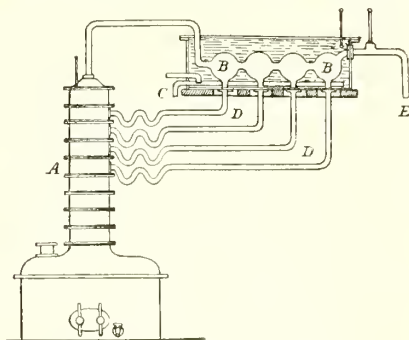


FIG. 15.

column A, there is a series of bulbs BB placed in a cistern containing brine, which may be heated by steam by means of the pipe C. The vapour—of benzene, for example—partially freed from

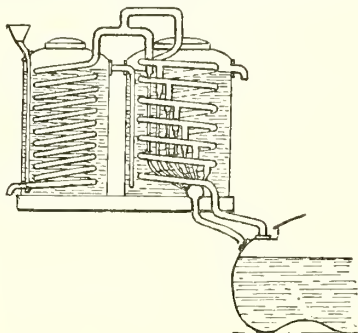


FIG. 16.

less volatile substances in the column, is further purified by partial condensation in the bulbs, the condensed liquid flowing back by the tubes BB

into the column, while the purified vapour passes on to the condenser by the pipe *e*.

Another form of partial condenser is shown in fig. 16. Other improvements have been devised in the apparatus required for the distillation of coal-tar products, but it is chiefly in connection with the distillation and rectification

of alcohol that the most notable advances have been made, and it is now possible to obtain alcohol of 95 p.c. in a single distillation from worts.

One of the earlier forms of apparatus is that of Pistorius (fig. 17). The wort is run from the pipe *a* into the heater *A*, thence by the pipe *bb*

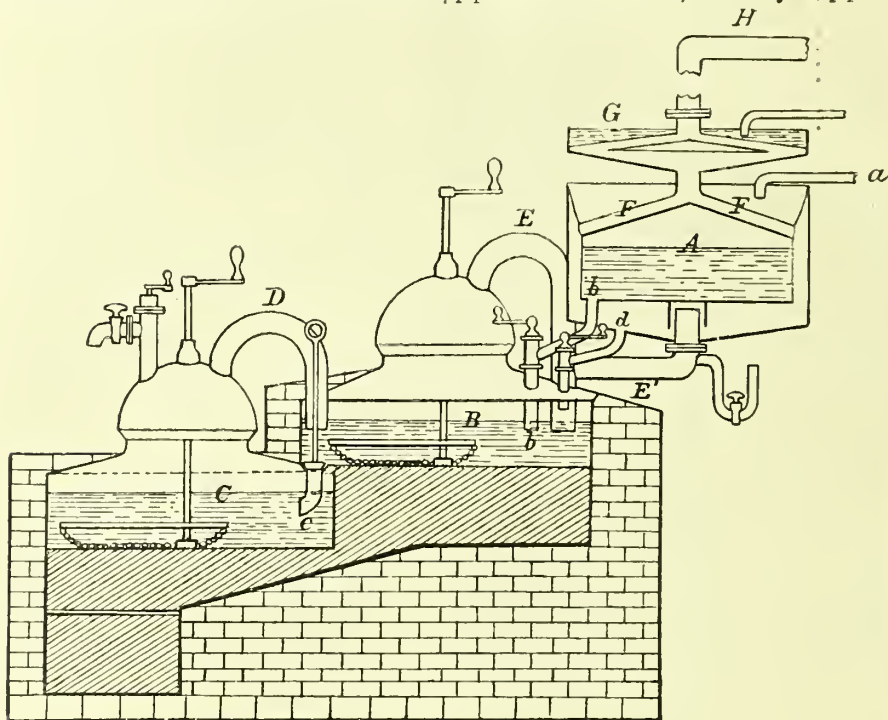


FIG. 17.

into *b*, and finally into *c* through the pipe *c*; *A* and *B* are then filled with wort. The still *c* is heated either by a furnace, as shown in the diagram, or by steam, the wort being constantly stirred by a chain. The weak alcoholic vapours pass through the pipe *b* into the second heater *B*, where they condense and heat the wort to the boiling-point, the waste heat from the furnace being also utilised. The stronger vapours from *B* now pass by the pipe *ee'* into the outer chamber of *A* (where more weak alcohol is condensed, and flows back into *B* by the pipe *d*) then up through the narrow passage *FF* into the dephlegmator *G*, shown on an enlarged scale in fig. 18. After passing through two or more of these dephlegmators the strong alcoholic vapour reaches the condenser by the pipe *h*.

For rectifying the spirit a still, known as the French column apparatus, may be used (fig. 19). The weak spirit is heated by a steam coil in *A*; the vapour is partially concentrated in the rectifier *B*, the construction of which is shown in fig. 20; it is then further freed from water in the condensing apparatus *C*, and finally reaches the condenser *D*.

In England the Coffey still is largely used; it differs considerably from those described, inasmuch as there is no large boiler, and the heat

is supplied, not from an outer fire or steam jacket, but by the condensation of steam in the wort; moreover, the process is continuous. The

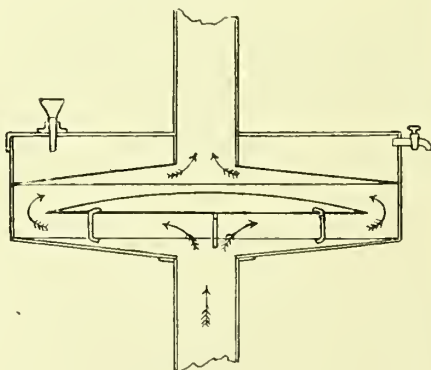


FIG. 18.

essential parts of the apparatus are shown in fig. 21. The wort is pumped from a reservoir *A* up the pipe *B*, and passes down the zigzag pipe *cc*, where it is heated by the ascending vapours,



then up the pipe *D*, from which it is discharged into the column *E*. It is prevented from falling

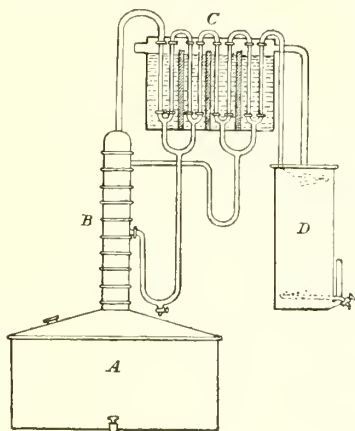


FIG. 19.

through the perforated plates of the column or analyser by the ascending vapours, but falls

through the pipes *FF* from one plate to another until it reaches the bottom, when it is allowed to escape. Meanwhile, steam is passed into the analyser *E* by the pipe *H*, and causes the wort to boil, so that by the time it has reached the bottom it is completely deprived of alcohol. The ascending vapours force their way through the perforated plates of the analyser, a portion of the aqueous vapour being condensed by each washing, and the descending wort being thereby heated. On reaching the top of the column the concentrated alcoholic vapour passes down the pipe *K* into the rectifier, and there ascends through similar perforated plates; but in the rectifier it is not washed by wort, but by the weak alcohol formed by the previous condensation of vapour. This dilute alcohol, on reaching the

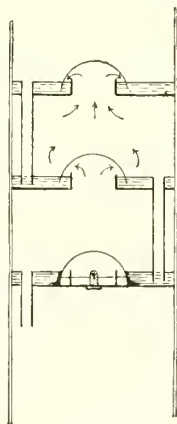


FIG. 20.

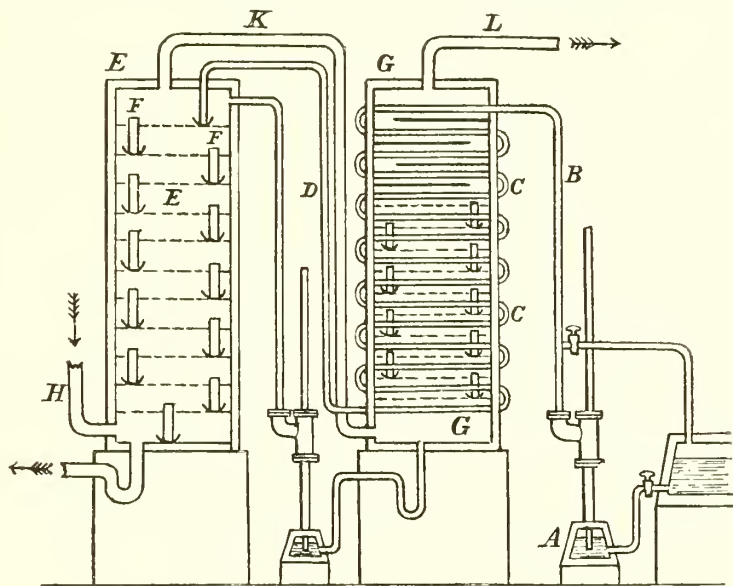


FIG. 21.

bottom of the rectifier, flows off into a reservoir, from which it is pumped into the top of the analyser, where it mixes with the descending wort. In the upper part of the rectifier there are simply shelves, which compel the vapour to take the same zigzag course as the pipe which conveys the wort downwards. The purified and concentrated vapour then passes through the pipe *L* to the condenser.

A great variety of stills are employed for the distillation of alcohol and other liquids, but the principles on which they are constructed are identical with those described.

S. Y.

**DITA BARK.** *Satween* (Ph. J. Trans. [3] 7, 110). *Alstonia scholaris*, *Echites scholaris*. The bark of *Echites scholaris*, a tree found in India, the Philippines, Eastern Australia, and tropical Africa (B. 11, 2234).

According to Harnack (B. 11, 2004; C. J. [2] 36, 332), it contains only one base, *ditaïne*, a basic glucoside, having the composition  $C_{22}H_{20}N_2O_4$ , but Hesse (A. 203, 144; B. 13, 1750; Ph. [3] 11, 251, 331) finds in it three bodies, *ditaïne*,  $C_{18}H_{19}NO_2$ ; *echitamine* (echitammium hydroxide),  $C_{25}H_{24}N_2O_4 + H_2O$ , melting with decomposition at  $236^\circ$ ; this base is identical with

Harnack's *ditaïne*; and *echitenine*  $C_{20}H_{27}NO_3$ , a brown amorphous mass, melting above  $120^\circ$ , soluble in chloroform, alcohol, and ether. It dissolves in nitric acid with the production of a purple-red colour which quickly passes through green into yellow.

The milky juice of this tree has the same properties as gutta percha; when inspissated it softens in boiling water, is soluble in turpentine and chloroform, and receives and retains impressions. The bark is thick and spongy (Oudaatze, Ph. [3] 13, 818). A decoction of the bark is used as an astringent tonic.

**DITAÏNE** *v.* DITA BARK; also VEGETO-ALKALOIDS.

**DIVI-DIVI.** The astringent seed-pods of *Cesalpinia coriaria*, a tree of twenty or thirty feet high, indigenous to the West Indies, Mexico, Venezuela, and Brazil. The pods are about two inches long, and three-fourths of an inch wide, flattened, and curiously curved, somewhat after the form of the letter S. By reason of the large quantity of tannin and ready-formed gallic acid contained in the husks they are largely imported for the preparation of leather, principally from Maracaibo, Paraiba, and St. Domingo. The material is also known as libi-divi and libi-dibi *v.* LEATHER.

**DOCIMACY** or **DOCIMASY.** (*Docimasia*, Fr.) Originally the act or art of examining by test (*δοκιμασία*, a test) applied in metallurgy to experiments made to determine the nature and purity of a metal; in pharmacy, to the testing of medicines and poisons; in medical jurisprudence, to the different proofs to which the lungs of a new-born child are subjected, for the purpose of ascertaining whether it was born alive or dead (Dunglison). Usually employed as synonymous with assaying.

**DODECATOIC ACIDS** *v.* FATTY ACIDS.

**DOEGLING TRAIN OIL** *v.* OILS.

**DOG-TOOTH SPAR.** The scalenohedral form of calc spar *v.* CALCUM.

**DOLomite.** A native carbonate of calcium and magnesium, named after Dolomieu, a French geologist of the last century. The mineral in its typical form contains equal molecules of the two carbonates, corresponding to 54.34 p.c. of  $CaCO_3$ , and 45.66 p.c. of  $MgCO_3$ . This variety is sometimes termed *normal dolomite*. Rammelsberg recognises two other varieties, occurring less frequently than the normal type, and containing respectively  $3CaCO_3$ ,  $2MgCO_3$  and  $2CaCO_3$ ,  $MgCO_3$ . But as the two carbonates are isomorphous, they occur associated in very variable proportions, and many of the massive dolomites are merely limestones more or less magnesian. It was maintained by Karsten and others that when dolomite contained more  $CaCO_3$  than the normal proportion, the excess might be dissolved out by cold acetic acid, leaving a dolomite of normal composition. Haushofer has shown, however, that the action of acetic acid cannot effect such a separation; at the same time he asserts that dolomite is not a true double salt, or homogeneous chemical compound (Sitzb. math.-phys. Cl. d. bair. Ak. München, 1881, Heft 11, 220).

Dolomite crystallises in the rhombohedral system; and, unlike calcite, it commonly assumes the primitive rhombohedron ( $106^\circ 15'$ ):

the forms are remarkable for presenting curved faces; while lenticular and saddle-shaped crystals are not unusual. Dolomite is slightly harder and denser than calcite; its H. being 3.5-4.5, and its sp.gr. 2.85-2.95. Its lustre is often naereous, especially in those varieties which contain a small proportion of  $FeCO_3$ , whence they are known as *pearl spar*. If the proportion of  $FeCO_3$  increases, the mineral assumes, on weathering, a brownish tint, and is sometimes termed *brown spar*.  $MnCO_3$  is often present to a slight extent, and imparts a faint pink tinge. Most varieties of dolomite show little or no effervescence with cold hydrochloric acid, but when powdered readily dissolve in the warm acid. Dolomite is soluble in water containing carbonic acid. The analyses of some of the dolomite springs in the Franconian Jura, by Gorup-Besanez, lead to the conclusion that natural waters acting on a normal dolomite may dissolve it, and re-deposit the mineral without decomposition. According to Bischof's experiments, the action of carbonated water on an imperfect dolomite, or dolomitic limestone, is to dissolve out the  $CaCO_3$ ; the rock becoming relatively richer in  $MgCO_3$  until a true dolomite is left; such a result, however, was not obtained by Gorup-Besanez (A. 8, Suppl. 1871, 230).

Some of the finest crystals of dolomite occur at Traversella in Piedmont; while in this country the best examples are obtained from the Laxey Mine, in the Isle of Man, from Derbyshire, Alston Moor, and Leadhills, in Lanarkshire. A variety of asparagus-green colour, from Miemo, in Tuscany, is termed *Miemitite*; it contains, according to Rammelsberg, 57.91 p.c. of  $CaCO_3$ , 38.97 of  $MgCO_3$ , 1.74 of  $FeCO_3$ , and 0.57 of  $MnCO_3$ . A compact snow-white variety from Gurhof, in Lower Austria, has been distinguished as *Gurhofite*.

Dolomite occurs not only as a mineral, but as a rock. Crypto-crystalline, granular, and compact varieties form mountain-masses of great magnitude, especially in the Eastern Alps, where they are largely developed in the triassic series, and form the characteristic jagged-peaked mountains known as 'the Dolomites.' Sterry Hunt has shown that a large proportion of the Canadian limestones should be classed as dolomites, and even where the rock is a normal limestone it is commonly veined with dolomite, while the fossils also are more or less magnesian; this is notably the case with the Trenton limestone of Ottawa, belonging to the Lower Silurian formation.

In this country magnesian limestone is developed on a large scale, especially in the Permian series, corresponding with the *Zechstein*, or Upper Dyas, of German geologists.

The outcrop of the magnesian limestone stretches, from the mouth of the Tyne, through Durham and Eastern Yorkshire, to the plain of the Trent near Nottingham. Certain beds near Sunderland are remarkable for presenting concretionary varieties, which assume globular and botryoidal forms, with a radiating structure, varying in size from a marble to a cannon-ball; while near Marsden there occurs a laminated variety, notable for yielding thin slabs which display flexibility. The massive and granular varieties have been largely quarried for ages as

a building-stone, the principal quarries being near Anston, in Yorkshire, Bolsover in Derbyshire, and Mansfield Woodhouse in Nottinghamshire. The best stone is of a warm creamy tint, easily worked, and when well selected extremely durable; the most durable kind being that which presents a crystalline texture and contains the two carbonates in molecular proportions, so as to form a normal dolomite. Southwell Cathedral, York Minster, and Ripon Cathedral, offer good examples of the use of this stone; and the perfection with which the Norman carving at Southwell had been preserved led to the selection of Bolsover dolomite as the stone for the New Houses of Parliament. According to Daniell, who analysed the Bolsover stone for the Commissioners appointed to make the selection, it contains 51.1 p.c. of  $\text{CaCO}_3$ , 40.2 of  $\text{MgCO}_3$ , 1.8 of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , 3.6 of  $\text{SiO}_2$ , and 3.3 of  $\text{H}_2\text{O}$ , &c. While this stone is, under ordinary circumstances, very durable, so large a quantity was required for the Houses that much of it was of inferior quality, and has not proved satisfactory; other localities than those originally selected were laid under contribution, and stone was thus introduced which has yielded to the disintegrating influences of a London atmosphere.

A rock known as *dolomitic conglomerate* occurs in the South-west of England and in South Wales, and appears to be an old beach deposit of Keuper age. It consists chiefly of pebbles and angular fragments of carboniferous limestone, united by a cement more or less magnesian and coloured with oxide of iron. The rock is quarried for burning, is used locally as a building stone, and when polished forms a handsome marble.

If magnesian limestone be calcined below a red heat, the carbonate of magnesium suffers decomposition while the calcium carbonate is but slightly affected. On slaking the product, the caustic magnesia forms a definite hydrate, which is said to unite with the unaltered carbonate of calcium to produce a cement that offers considerable resistance to the action of water. Magnesian limestone if argillaceous, though only to a small extent, has the reputation of forming good hydraulic cement; but some authorities allege that after a time the magnesian cements suffer alteration whereby their durability is greatly impaired. If dolomite be perfectly calcined, the product may be used for taking casts, since it 'sets' with water, like gypsum, though but very slowly.

Calcined dolomite is extensively employed as a lining for the converters used in the basic method of steel-manufacture, invented by Thomas and Gilchrist. The calcination is effected in either cupolas or regenerative kilns. After nine hours' burning, the stone, though still hard, is found to have lost about half its volume and half its weight. This 'shrunk dolomite' is crushed, mixed with gas-tar as a vehicle, and moulded into bricks, which are then heated until the tar is burnt off, when they are ready for use in the converter.

Dolomite treated with sulphuric acid yields the sulphates of calcium and magnesium, the two salts being readily separated by the greater solubility of the latter; hence magnesian lime-

stone has been largely employed as a source of Epsom salts.

The origin of dolomite has given rise to much discussion, and probably more than one natural mode of formation must be recognised. While the frequent occurrence of dolomite with rock-salt and gypsum, and the paucity of associated fossils, suggest that it has been formed in inland waters, there are difficulties in the way of admitting its formation by direct precipitation. Sterry Hunt suggests that  $\text{Na}_2\text{CO}_3$ , resulting from the decomposition of soda-bearing minerals, like certain feldspars, might be carried by fresh waters to the sea, and on meeting with  $\text{CaCl}_2$  and  $\text{MgCl}_2$  decomposition would ensue, with formation of  $\text{NaCl}$  and  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . To account for the association of dolomite with gypsum he assumes a reaction between  $\text{CaCO}_3$  and  $\text{MgSO}_4$  whereby  $\text{CaSO}_4$  and  $\text{MgCO}_3$  would be formed, and the latter might associate itself with fresh  $\text{CaCO}_3$  to form the double carbonate. Most dolomite seems, however, to have been formed by the alteration of limestone. Water holding carbonate of magnesium in solution may cause the dolomitisation of a limestone through which it happens to percolate. The replacement of a molecule of  $\text{CaCO}_3$  by one of  $\text{MgCO}_3$ , so as to form a dolomite, is accompanied by a diminution of volume to the extent of 12 or 13 p.c.; and it is characteristic of many dolomites to possess a cavernous structure. Elie de Beaumont suggested that this is due to the shrinkage consequent on dolomitisation; while Von Morlot found by direct observation that the cavities in such a rock amounted to 12.9 p.c. of its bulk. It must be remembered that most limestones of organic origin, such as coral limestones, are more or less magnesian, and Richthofen and others hold that many of the Tyrolese dolomites are altered coral-reefs. It was formerly supposed that the dolomites of Tyrol were limestones which had been metamorphosed by heated magnesian vapour emitted from eruptive rocks; and Durocher found that by heating fragments of limestone with  $\text{MgCl}_2$  they became partially dolomitised. It is much more probable, however, that the alteration has been effected by the magnesium salts in sea-water. V. *Chemisch-genetische Beobachtungen ü. Dolomit*, by C. Doelter and R. Hoernes, *Jahrb. d. k.-k. geolog. Reichs.* 25, 1875, 293 (containing numerous analyses of dolomites of S.E. Tyrol, and a copious bibliography of dolomite). V. *CALCIUM and MAGNESIUM*.

F. W. R.

**DOMEYKITE.** A copper arsenide containing  $\text{Cu}_3\text{As}$ , corresponding to copper 71.7, and arsenic 28.3 p.c. It occurs in reniform, botryoidal, and compact masses, of white or grey colour, with metallic lustre, rapidly tarnishing.  $H. = 3-3.5$ ; sp.gr. 7-7.5. Readily fusible before the blowpipe, with emission of arsenical vapours. Soluble in nitric acid, but not in hydrochloric acid. It is found at Coquimbo and Copiapo in Chile, at Cerro las Paracatas in Mexico, and at Zwickau in Saxony. The following are analyses from the principal localities:

	I.	II.	III.	IV.
Cu . . .	71.64	71.48	71.13	65.08
As . . .	28.36	28.26	28.41	26.45

I. From Chile, by Domeyko, after whom the species is named.



- II. From Coquimbo, Chile (F. Field).  
 III. From Corocoro, Bolivia (D. Forbes); this contained 0.46 p.c. Ag.  
 IV. From Zwickau (A. Weisbach); this contained 0.64 Fe, 0.44 Ni, 2.49 O, and 3.84 residue; the oxygen indicates partial decomposition (J. M. 1882, 2, 249).

Several other arsenides of copper, more or less like domeykite, are known. The *Algodonite* of F. Field contains  $\text{Cu}_3\text{As}$ , and occurs at the Algodones Mine, near Coquimbo. *Whitneyite*, from Houghton Co., Michigan, U.S., described by F. Genth, contains  $\text{Cu}_3\text{As}$ ; and D. Forbes's *Darwinite*, named after Charles Darwin, is a similar mineral from near Copiapo. The *Condurrite* of Faraday, from Condurrow Mine, Cornwall, appears to be a mixture of arsenide of copper with various oxidised products derived from the alteration of tennantite or some kindred species. F. W. R.

#### DOUBLE SCARLET v. AZO-COLOURING MATTERS.

**DRAGON'S BLOOD.** A resin used as a red pigment (v. **PIGMENTS**; also **RESINS**).

**DROP GUM, or GAMBOGE, v. PIGMENTS.**

**DRUMINE.** An alkaloid stated to be present in *Euphorbia Drummondii* (Ogston, Brit. Med. Journ. 1887, 451).

**DRYOBALANOPS CAMPHOR v. CAMPHOR.**

**DULCAMARA.** *Bittersweet*, *Woody Nightshade*. (*Douce amère*, Fr.; *Bittersüss*, Ger.) The young branches of the *Solanum Dulcamara* (Linn.), a climbing plant with purple flowers and red berries inhabiting the British Islands and most parts of Europe (Woodville, Med. Bot. 33; Benth. a. T. 190). The drug appears to be going out of use; but in the form of decoction it is sometimes administered as a remedy in rheumatism and certain skin diseases.

The investigations of Pfaff (Mat. Med. 6, 506), Desfosses (J. Ph. 6, 414), Pelletier (J. Ph. 6, 416), and others went to show that bittersweet contained a glucoside 'dulcamarin,' 'piroglycion,' or 'dulcarin,' and also a compound believed to be the alkaloid 'solanine' (cf. Meissonier, A. 1, 368). Continuing an inquiry of Wittstein's (Vierteljahrs. pr. Pharm. 1, 364, 495), Geissler has shown (Ar. Ph. [3] 6, 1010) that dulcamara contains a definite compound *dulcamarin*  $\text{C}_{22}\text{H}_{31}\text{O}_{10}$ , together with a substance resembling solanine, which, however, does not yield sugar when heated with dilute acids. The *dulcamarin* of Geissler is a slightly yellow, inodorous, amorphous powder having a strong bitter taste, followed by sweetness. It is soluble in water and alcohol, but insoluble in ether, chloroform, and benzene. It forms a lead salt  $\text{C}_{22}\text{H}_{32}\text{PbO}_{10} \cdot 5\text{H}_2\text{O}$ . With dilute sulphuric acid it breaks down into *glucose* and *dulcamaretin*  $\text{C}_{16}\text{H}_{21}\text{O}_8$ ; thus  $\text{C}_{22}\text{H}_{31}\text{O}_{10} + 2\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_{16}\text{H}_{21}\text{O}_8$ . *Dulcamaretin* is resinous, and forms the lead salt  $\text{C}_{16}\text{H}_{21}\text{PbO}_8$ . A. S.

**DULCITOL.** *Dulcin*, *Dulcose*, *Melampyrite*, *Melampyrin*. A hexatomic alcohol,  $\text{C}_6\text{H}_{14}$ ;  $:(\text{OH})_6$ .  
*Occurrence.*—Found in a manna or crude preparation from a bulbous root of unknown origin from Madagascar (Laurent, Compt. Chim. 1850, 364; 1851, 29. Jacquelin, *ibid.* 1851, 21), in *Scrophularia nodosa* and *Rhinanthus Crista galli* (Eichler, Ueb. d. Melampyrin, Moscow, 1885); in *Melampyrum nemorosum*

(Hünefeld, J. p. Chem. 4, 233; Gilmer, Ann. Chem. Pharm. 123, 372); in *Euonymus europæa* (Kubel, J. p. Chem. 85, 372), and in *dulcitra manna* (Hecht, Ann. Chem. 165, 148).

*Formation.*—By the action of nascent hydrogen (sodium amalgam) on lactose or galactose, and no doubt by that of the same reagent on all galactose-yielding bodies, Bouchardat (Ann. Chim. [4] 27, 79; C. R. 73, 199; 74, 665, and 1406; Bl. [2] 18, 115).

*Preparation.*—Dulcitol is prepared from the Madagascar material by extracting with boiling water and allowing the filtrate to crystallise. To prepare it from the plants above mentioned they are gathered at a suitable time and dried. A decoction is made of them, rendered alkaline with milk of lime, boiled, filtered, concentrated, and acidified with hydrochloric acid. Dulcitol crystallises out on cooling. Or, an extract is made of the dried plants with dilute hydrochloric acid. This is strained and rendered slightly alkaline with milk of lime and concentrated; calcium succinate crystallises out and is separated by filtration. The filtrate contains the calcium compound of dulcitol; on slight concentration and addition of hydrochloric acid, crystals of the body are deposited which may be purified by recrystallisation (Eichler), or the decoction is precipitated with lead acetate, the filtrate digested with lead oxide, the excess of lead is removed from the solution by hydrogen sulphide. The filtrate on concentration yields a full crop of crystals. The decoction of the dried plants on evaporation to a syrup deposits dulcitol (Hünefeld), and he obtains a further yield by treating the mother liquors with lead acetate and sub-acetate removing excess of lead from the filtrate by hydrogen sulphide and concentrating. *Dulcitra manna* is extracted with boiling alcohol; dulcitol crystallises from the solution filtered hot. The manna yields 72 p.c. dulcitol (Hecht).

To an aqueous solution of lactose, galactose, or inverted lactose, sodium amalgam, containing about 2 p.c. sodium, is gradually added, the soda produced being from time to time neutralised with sulphuric acid. When hydrogen is evolved in large quantities instead of being taken up, the alkali is carefully neutralised with sulphuric acid and the sodium sulphate allowed to crystallise out. This is removed, and the filtrate concentrated, when more sodium sulphate crystallises; a further quantity can be separated by strong alcohol. From the concentrated solution dulcitol separates in small, crystalline, warty groups, which can be purified by draining and recrystallising from water (Bouchardat).

*Properties.*—Dulcitol crystallises in colourless, highly lustrous monoclinic prisms with octahedral summits. The body from the Madagascar source, that obtained from *Melampyrum nemorosum*, and that produced by the action of sodium amalgam on galactose, crystallise in forms which yield practically the same measurement. The crystalline habitus of the body is that of aggregated crusts; separate crystals with well-defined terminations have also been observed. The crystals are gritty between the teeth and taste very faintly sweet. F.p. 186-188, but the authorities differ slightly. One part

dulcitol dissolves in 34.41 parts water at 16.5° (Erlenmeyer and Wanklyn, J. C. 15, 455). It is but slightly soluble in alcohol even at a boiling temperature, and acetone, wood spirit, chloroform, and ether dissolve but little of it. It is slightly, if at all, optically active. Its solutions are not coloured brown by potash, nor do they reduce alkaline copper solutions. Nitric acid oxidises it to mucic acid, oxalic and racemic acids are also produced (Carlet, C. R. 51, 137; 53, 343). *Saccharomyces* forms do not ferment it, but other organisms such as exist in cheese, and may grow in a suitable medium, convert it, in presence of calcium carbonate, into alcohol, lactic, and butyric acids. In contact with testicular tissue it yields a peculiar sugar (Berthelot, Ann. Chim. [3] 50, 348 and 372). When dulcitol is heated at 140° with more than 6 mols. phosphorus pentachloride and the product distilled in steam, a slightly yellowish oil  $C_6H_5Cl$  is obtained; this when heated with hydriodic acid and amorphous phosphorus gives a volatile hydrocarbon, probably hexane (Bell, B. 12, 1271). A saturated solution containing dulcitol and borax in the proportion of 2 mols. dulcitol to 1 mol. borax is neutral, but if the proportion of borax is less, the solution is strongly acid, when the proportion of borax is greater the solution is alkaline (dulcitol being neutral and borax slightly alkaline). A solution of a mixture of dulcitol and sodium paratungstate has an acid reaction after boiling (Klein, C. R. 99, 144).

Dulcitol sublimes partially on careful heating; at 200° it gives off water, and is converted into *dulcitan*, at 275° it decomposes with evolution of carbon monoxide and without much colouring. When the temperature is increased, large quantities of gas are given off with the odour of acetic acid and acetone, and without leaving a residue.

Solutions of salts do not precipitate dulcitol, but compounds with the bases have been described.

An ammonia compound is obtained in colourless rectangular prisms by decomposing the calcium or barium compound of dulcitol with ammonium carbonate and concentrating the filtrate, or by decomposing nitro-dulcitol with ammonium sulphide and concentrating.

Sodium, potassium, and calcium compounds exist. Barium compound  $C_6H_{11}O_6 \cdot BaO \cdot 7H_2O$  is obtained by heating molecular proportions of barium hydroxide and dulcitol in strong solution. On cooling, prismatic crystals of this composition are deposited. They part with half their water over sulphuric acid.

A copper compound is produced as a light-blue precipitate when an ammoniacal solution of copper sulphate is added to an aqueous solution of dulcitol.

Neither lead acetate nor subacetate precipitate dulcitol, but a white precipitate is thrown down with an ammoniacal solution of acetate. This is an unstable lead compound.

Dulcitol heated with hydriodic acid in an atmosphere of carbon dioxide yields hexyl-iodide, water, and iodine



Dulcitol yields two nitro-derivatives, viz., hexanitro-dulcitol  $C_6H_3(NO_2)_6O_6$ , and a tetra-nitro-dulcitol  $C_6H_9(NO_2)_4O_6$  (Béchamp, C. R. 51, 257). These bodies appear to partake rather of the

character of nitrates than nitro-compounds, the former being dulcitol hexanitrate  $C_6H_3(NO_2)_6O_6$  and the latter dulcitol tetranitrate  $C_6H_9(NO_2)_4O_6$ . The hexanitrate is obtained by the action of fuming nitric and sulphuric acids on dulcitol. It crystallises from alcohol in beautiful colourless flexible needles which melt between 68° and 72°, and give off nitric acid vapours continually, being thereby converted into the tetranitrate. This latter is soluble in alcohol, from which it crystallises in translucent prisms, m.p. 130°–140°, and decomposed at 145°.

Dulcitol forms with hydrochloric acid an unstable hydrochloride  $C_6H_{11}O_6 \cdot HCl \cdot 3H_2O$ . Similar hydro-bromides and hydro-iodides exist; they are rather more stable bodies (Bouchardat, Ann. Chim. [4] 27, 145).

Dulcitol yields chloro- and bromo-hydrins as well as a chloro-bromo-body.  $C_6H_{12}O_4Cl_2$  crystallises in tables insoluble in water;  $C_6H_{12}O_4Br_2$  and  $C_6H_{12}O_4BrCl$  are of much the same nature. The corresponding dulcitan bodies  $C_6H_{11}O_4Cl$ , &c., exist. When these bodies are dissolved in fuming nitric or sulphuric acids the corresponding tetra-nitrates are formed, as  $C_6H_3Cl_2(NO_2)_4O_6$ , &c.

With sulphuric acid dulcitol yields a conjugate acid the barium salt of which is soluble. Dulcitol is dissolved in strong sulphuric acid and the solution neutralised with barium carbonate. The filtrate from the barium sulphate can be evaporated in a vacuum to a thick syrup which over sulphuric acid dries up to a transparent gum. The composition of the acid is probably  $C_6H_5O_4(SO_3H)_3$ , and the barium salt contains 36.45 p.c. BaO, and 37.79 p.c.  $SO_3$ . The calcium salt is similar to the barium one. Dulcitan sulphuric acid is formed by the action of chloro-sulphonic acid on dulcitol (Cläesson, Sitzungsber. 201, 15).

With the acids of the fatty and aromatic groups, dulcitol forms a number of neutral compound ethers. Some of these are ethers of dulcitol and some of dulcitan; for example, with acetic acid we have:

*Di-aceto-dulcitol*  $C_6H_8 \begin{Bmatrix} (OC_2H_3O)_2 \\ (OH)_1 \end{Bmatrix}$   
crystalline scales, m.p. 176°, converted into acetic acid and dulcitol by alkalis.

*Di-aceto-dulcitan*  $C_6H_8 \begin{Bmatrix} (OC_2H_3O)_2 \\ (OH)_2 \\ O \end{Bmatrix}$

a thick colourless liquid, soluble in water, alcohol, and ether  $[\alpha_D] = +1.52^\circ$ .

*Hexaceto-dulcitol*  $C_6H_4(OC_2H_3O)_6$ . Hard crystalline plates, m.p. 171°; sublimes at 200–220°. The product for a time differs slightly from the original body.

*Tetr-aceto-dulcitan*  $C_6H_8 \begin{Bmatrix} (OC_2H_3O)_4 \\ O \end{Bmatrix}$   
a colourless resin which sublimes without residue,  $[\alpha_D] = +6.52$ .

*Pent-aceto-monochloro-dulcitol*  
 $C_6H_8 \begin{Bmatrix} (OC_2H_3O)_5 \\ Cl \end{Bmatrix}$

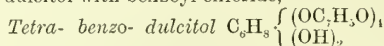
an unstable body obtained by the action of a mixture of acetic and hydrochloric acids on dulcitol. When heated with water it yields hydrochloric acid and

*Pent-aceto-dulcitol*  $C_6H_8 \begin{Bmatrix} (OC_2H_3O)_5 \\ OH \end{Bmatrix}$



a crystalline body converted by heating for a long time at 200° into an aceto-dulcitan.

A like series of bodies is obtained by acting on dulcitol with benzoyl chloride,

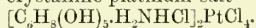


is a resinous precipitate converted into tetra-benzo-dulcitan by heating to 140°.

*Hexa-benzo-dulcitol*  $C_6H_5(OC_6H_5O)_6$  crystals insoluble in water and ether, slightly soluble in alcohol, m.p. 147°. A mixture of nitric and sulphuric acids converts it into *Hexa-nitro-benzo-dulcitol*.

With phenyl cyanate, dulcitol yields dulcitol phenyl carbamate  $C_6H_5O \left\{ \begin{array}{l} (CO.NHC_6H_5)_5 \\ (OH) \end{array} \right.$  m.p. 250-252° (Tessmer, B. 18, 971).

When the different dulcitol or dulcitan hydrins are treated with ammonia, dulcitol amine is produced. This is strongly basic; it is amorphous. The hydrochloride crystallises in needles; it yields a crystalline platinum salt



O'S.

**DUMONT'S BLUE.** *Smalt v. COBALT*; also PIGMENTS.

**DUNGING-SALT.** *Sodium arsenate v. ARSENIC.*

**DURENE** *v. CYMENES.*

**DUTCH BUTTER** *v. MARGARENE.*

**DUTCH PINK**, or **ITALIAN PINK**, *v. PIGMENTS.*

**DUTCH ULTRAMARINE.** *Cobalt blue v. COBALT and PIGMENTS.*

**DYEING.** The art of dyeing consists in imparting colour to various substances, more especially the textile fibres, in such a manner that it is not readily removed or altered by those influences to which the dyed material is subsequently exposed. Dyeing differs from mere staining, in that the colour imparted is of a more permanent character by reason of the pigment being more intimately united with the material dyed; it differs also from painting, since the colouring matter is not applied to the surface only, but penetrates more or less the material dyed, and thus leaves its structural appearance unchanged except in colour.

The methods employed in dyeing vary according to the nature of the fibre or other material and the colouring matter employed. The various textile fibres show remarkable differences of behaviour towards one and the same colouring matter. Wool and silk, and, indeed, animal substances generally, *e.g.* horn, feathers, &c., behave somewhat similarly towards colouring matters, and are more readily dyed than cotton or linen and most other vegetable substances. The fundamental cause of this difference is not yet satisfactorily explained, and opinion is still divided on the question of the relative importance of the physical structure and the chemical composition of the various fibres.

The supporters of what may be termed the *mechanical theory of dyeing* urge that there is no sufficient evidence that the fibre and colouring matter combine according to chemical equivalents, and further, that neither of them has lost its characteristic physical and chemical properties. Colouring matters can in many cases be very readily removed by alcohol or other

solvents from the fibres; the latter then apparently show no change from their original structure and condition. The dyeing of wool and silk has been compared with the attraction or solvent action exerted by ether when it withdraws a colouring matter from an aqueous solution with which it is well agitated. The textile fibres are considered to exert a purely physical attraction towards colouring matters, and the latter are supposed to be held in an unchanged state within and upon the fibre. The differences in attraction exhibited by the various fibres are ascribed to their different degrees of porosity. The question is regarded, indeed, as one of molecular surface attraction very similar to, if not identical with, that exercised by animal charcoal when it decolourises a coloured solution during filtration. In some cases of dyeing this seems to be the only tenable view, *e.g.* in dyeing cotton with indigo by the vat method, when by exposure to the air the colourless indigo-white solution absorbed by the fibre is changed into insoluble indigo-blue, which is thus precipitated upon and possibly also within the fibre. The dyeing of Prussian blue, chromate of lead yellow, &c., on cotton presents similar features.

Certain facts, however, seem to favour the *chemical theory of dyeing*, particularly with respect to the dyed animal fibres, according to which they may be regarded as chemical compounds analogous to salts, in which the fibre plays sometimes the part of an acid, at others that of a base, just as alumina and stannous oxide behave towards strong acids or bases. Wool and silk, for example, may be dyed red in a solution of the colourless base rosaniline, and yet this body otherwise only produces colour when it is combined with an acid. Further, when wool is dyed in a solution of rosaniline hydrochloride (magenta), the latter undergoes decomposition, the rosaniline is taken up by the fibre, and the whole of the hydrochloric acid is found in the waste dye solution. In these cases, therefore, wool and silk seem to play the part of acids, and produce an insoluble coloured compound with the base rosaniline.

Again, with respect to certain colouring matters of a marked acid character, *e.g.* the sulphonic acid azo-colours, the animal fibres appear to play the part of a base. Not being able to decompose the commercial alkali salts of the sulphonic acid colours, these fibres do not become dyed in a solution of the commercial colours, but they readily dye if the colour-acid is liberated by adding a mineral acid to the dye bath. If the free colour-acid possesses a different colour from its alkali salt the dyed fibre nevertheless possesses the colour of the alkali salt, a further point in favour of the basic behaviour of the fibre and its combination with the colour-acids in such cases.

Experiments (which have been recently made) also tend to show that the chemical theory of dyeing may be the true one as regards wool and silk. Wool seems to absorb from very concentrated solutions of acid and basic coal-tar colours definite maximum amounts of colouring matter which bear more or less simple molecular relationships to each other.

Further, by the action on wool of sulphuric acid, caustic alkalis, or even water at 200°C., an



albuminoid substance termed lanuginic acid is produced, which in its general dyeing properties behaves very like wool. With metallic salts, basic and acid coal-tar colours, it yields precipitates of definite chemical composition, and Knecht puts forward the hypothesis that lanuginic acid, or rather some insoluble modification of it, forms a constituent of wool to the extent of about 30 p.c. of its weight, and thus he explains chemically by its means all the reactions which take place during the mordanting and dyeing of this fibre. A similar hypothesis may be applied to silk.

Another fact in favour of the existence of a chemical union between colouring matter and fibre in some cases is that when the chemical composition of a fibre is altered its behaviour towards colouring matter is also different. Nitro-cellulose and oxy-cellulose, for example, possess a much greater attraction than cellulose for basic colouring matters (magenta &c.).

With colouring matters which can only be fixed upon fibres by the aid of mordants, the question is merely transferred to the nature of the attraction existing between fibre and mordant, for the union of the latter with the colouring matter is undoubtedly in most cases of a truly chemical character. With alizarin-red dyed cotton, for example, the alumina mordant is probably physically attracted by the fibre but chemically combined with the alizarin. With tannin mordanted cotton, most probably a physical attraction exists between the tannic acid and the cellulose.

From the foregoing statements it seems probable that no single theory of dyeing is applicable in all cases, and although with our present knowledge we are not able to explain to our complete satisfaction the fundamental cause of dyeing, there seems to be reasonable ground for considering that in some cases a chemical attraction is exerted between colouring matter and fibre, *e.g.* in the case of wool and silk, and that in others a physical attraction is exerted, *e.g.* in the case of cotton.

With respect to the seat of the colouring matter in dyed fibres, it differs according to the fibre, colouring matter, and method of dyeing. As a rule, dyed wool and silk are permeated more or less throughout their substance with the colouring matter; in dyed cotton the substance of the fibre is sometimes permeated with colour in a similar manner, but frequently it is fixed almost entirely on the surface.

*Classification of colouring matters.*—The dyestuffs at present employed exhibit marked differences in their physical and chemical properties, and from the point of view of the former they may be divided into two large groups, *viz.* *pigments* and *colouring principles*.

The essential characteristic of the *pigments* is that they possess a more or less intense and fully-developed colour in themselves; they are coloured bodies, and need only, as it were, to be fixed in a more or less unchanged condition upon the textile fibres. To this group belong magenta, indigo, azo-scarlet, &c. A noticeable feature of this class of colours is that they yield at most various tones of one colour; they are *monogenetic*.

The mode of applying them to wool and silk and animal substances generally is usually

very simple. It suffices in most cases to steep the material to be dyed in hot solutions of the colouring matter with the addition of some acid, alkali, or salt. Their application to the vegetable fibres is frequently of a more complex character, and will be referred to afterwards.

The characteristic feature of the *colouring principles* is that they possess little or no colour in themselves, and are only useful as dyestuffs because they are capable of combining with other substances to produce intensely coloured bodies or pigments, which may be permanently fixed upon the textile fibres. When such coloured bodies are produced apart from the fibres they are termed *lakes*. Very many colouring principles are capable of yielding several differently coloured pigments according to the substance with which they are combined, and such may therefore be termed *polygenetic* colouring principles. To this group belong alizarin (madder), carminic acid (cochineal), brazilin (peachwood), &c.

The application of this class of dyestuffs both to the animal and vegetable fibres generally comprises two operations, *viz.* *mordanting* and *dyeing*. The first has for its object the fixing upon the fibre in an indelible manner the *mordant*, *i.e.* that substance which combines with the colouring principle to produce the requisite coloured pigment. The dyeing operation, which usually follows that of mordanting, consists in the application of the colouring principle.

The terms *adjective* and *substantive* colouring matters introduced by Bancroft refer to those which are applied by the aid of a mordant and those which are applied directly; they coincide somewhat with the terms colouring principles and pigments used here, but not entirely so. The latter terms refer to the presence or absence of fully-developed useful colour in the substance itself, while the former terms indicate merely the method of application, and since this varies according to the nature of the fibre, it frequently happens that a colouring matter may be substantive towards wool and silk, and adjective towards cotton. This is the case, for example, with magenta and similarly constituted colouring matters.

Another mode of classifying the numerous dyestuffs is that based upon their chemical character, and although this plan leads to an arrangement of numerous sub-divisions, it marks out two or three prominent groups, a consideration of which will demonstrate certain fundamental facts connected with the application of colouring matters. If the colouring principle alizarin and the pigment magenta are compared with each other with regard to their general chemical composition, no analogy is apparent, but if the ultimate dyed colour or pigment alizarin-red be compared with magenta, the case is different. Alizarin-red consists of a colouring principle (alizarin) combined with the base (alumina), while magenta is composed of a colouring principle (rosaniline) combined with the acid (hydrochloric acid).

Alizarin and rosaniline are indeed types of two large groups, *viz.* *acid* and *basic colouring principles*, and these require to be combined with substances of an opposite chemical character in order to yield a coloured body, pigment, or dye;

the former require the aid of basic mordants (metallic oxides), the latter that of acid mordants (tannic acid). This necessity applies to both, when considering their application to cotton, but with respect to wool it only holds good with the former, for it has already been pointed out that wool and also silk may be dyed directly with the base rosaniline alone. If, however, as has been suggested, these fibres themselves act as acid mordants, this behaviour of the basic colouring principles towards wool and silk is at once explained, and does not constitute a real exception to the above statement.

Acid colouring principles like alizarin are really of a phenolic character, and are employed in the free state, whereas it is customary to use the basic colouring principles in combination with acids, *i.e.* as salts. Although the latter then appear as soluble pigments, their true character as basic colouring matters is not recognised until it is attempted to apply them to the cotton fibre, when it is found that they are not directly applicable, but require the aid of an acid mordant, *viz.* tannic acid, &c.

Another large group comprises the *sulphonic acid colouring matters*, *viz.* soluble pigments in which the presence of the sulphonic acid group ( $\text{HSO}_3$ ) is the characteristic feature. Most of these are employed in the form of sodium salts, and are only applicable to the animal fibres, these being simply dyed in aqueous solutions with the aid of a little sulphuric acid. This addition is necessary in order to liberate the free sulphonic acid for which alone the fibre has any attraction. Since, however, it is necessary to add a larger amount of acid than is required for this purpose, E. Knecht considers that the excess assists in the production within the wool fibre of the lake-giving substance lanuginic acid above referred to. Typical representatives of this class are, indigo-extract, crocein-scarlet, acid-magenta, &c. This group includes, however, an ever increasing series of sulphonic acid colouring matters which differ in a remarkable manner from those just referred to, since they not only dye wool and silk in a neutral or slightly alkaline bath, but are directly attracted by cotton. Representatives of this class are: Congo red, chrysamin, &c. Another group of some importance is that comprising pigments which contain the nitro-group ( $\text{NO}_2$ ). They are of an acid character, and possess dyeing properties very similar to the first mentioned sulphonic acid colouring matters referred to above. Picric acid and aurantia are representative members of this group.

Other subsidiary groups of colouring matters will be referred to subsequently; it is only intended here to draw attention to the fact that an intimate relation exists between the chemical constitution of a colouring matter and its method of application.

**Mordants.** These are substances whose particular function it is to fix colouring matters upon textile materials. It has already been pointed out that they are specially needed with colouring principles having a marked acid or basic character, in which case they also develop the required colour. Their action is of a chemical nature; they produce with the colouring principles insoluble coloured compounds, and pre-

cipitate these within or upon the fibre. The mode of applying the mordants varies according to the fibre, colouring matter, and mordant employed.

*a. The most important class of mordants is that comprising the metallic salts, which as basic mordants are employed with all fibres in conjunction with acid colouring principles of a phenolic character, e.g. alizarin.*

Wool is mordanted by boiling it with dilute solutions of these metallic salts, usually with the addition of certain acids or acid salts, *e.g.* cream of tartar, oxalic acid, &c. During this operation the wool assists in the dissociation of the metallic salt, an insoluble basic salt being fixed within and upon the fibre, while a more acid salt remains in solution. According to E. Knecht the mordant is fixed as an insoluble compound of lanuginic acid. The acids or acid salts, which are added along with the mordant or metallic salt, possibly assist the dissociation of the latter by forming more sensitive salts (tartrates, oxalates, &c.), and may be conveniently termed *assistants*.

As a rule the mordanting operation precedes that of dyeing; not unfrequently, however, the two operations take place simultaneously, and the dyeing is thus effected by the so-called 'single bath,' 'one dip,' or 'direct' method, as, for example, in dyeing wool cochineal scarlet. In such cases the wool is boiled in a solution containing colouring matter, metallic salt, and assistant, in certain accurately determined relative proportions. Combination takes place between the colouring matter and the mordant, but the pigment which would otherwise be precipitated is retained in solution by the liberated acid of the mordant or the assistant present, and is only withdrawn from the solutions by the fibre gradually, or attracted and rendered insoluble by the lanuginic acid of the fibre, which thus becomes dyed.

In some cases the application of the mordant succeeds that of the colouring matter. This constitutes the so-called 'saddening method' of dyeing, because it is usually only adopted with those mordants which give sad or sombre colours (*e.g.*  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ ). Only a very limited number of dyestuffs give really good results by this method, *viz.* camwood, barwood, sanderswood, and catechu, since most colouring matters are not attracted in sufficient quantity by the fibre alone, to yield full rich colours when subsequently developed by combination with the mordant applied. Experiment shows that the colouring matters of these dyestuffs are attracted by, and form insoluble compounds with, lanuginic acid.

*Silk* is mordanted in the same manner as wool, by boiling with metallic salt solutions; or it is simply steeped for twelve hours or so in cold solutions of the salts previously rendered more or less basic and sensitive. By subsequently washing with water, preferably calcareous, the metallic salt absorbed by the silk is dissociated, and an insoluble basic salt, or one analogous to the insoluble compound of lanuginic acid above referred to, is precipitated within the fibre.

*Cotton* is mordanted with metallic salts by processes very different from those adopted for wool and silk, because it has not the property



of causing the dissociation of the metallic salts by boiling in their solutions. The methods to be adopted vary, also, according to the form of the material, *i.e.* whether it be cotton-wool, yarn, or cloth.

With calico it is usual to impregnate the fabric with solutions of metallic *acetates*, then to dry it, and expose for several hours to a moist warm atmosphere. During this so-called 'ageing' process, dissociation of the salt takes place, acetic acid escapes, and a more or less basic salt remains fixed upon the fibre.

Sometimes the 'ageing' is replaced by a 'steaming process,' in which the fabric is exposed from  $\frac{1}{4}$ –1 hr. in a closed chamber to the action of high or low pressure steam. This method is adopted by the printer of textile fabrics in the so-called 'steam style,' in which a mixture of colouring matter and metallic salt (usually acetate) is printed upon the fabric, which is then dried and steamed. The metallic salt is decomposed, a basic salt is precipitated upon the fibre, at the same time combining with the colouring matter and producing the coloured pigment. This method is analogous to the single-bath process of the woollen dyer.

Cotton may also be mordanted by impregnating it with metallic salt solutions, drying, and then passing through solutions of such alkaline substances as neutralise the acid and precipitate upon the fibre a basic salt or the metallic oxide, *e.g.* ammonia, chalk, sodium carbonate, &c. One may also use solutions of those alkali salts whose acids form insoluble compounds with the base of the mordant, *e.g.* sodium phosphate, silicate, arsenate, &c. All substances used in this manner for fixing the mordant upon the fibre are termed *fixing-agents*.

In some cases of mordanting, the cotton is impregnated with the fixing-agent first (*e.g.* tannic acid, sulphated-oil, &c.), then dried and passed through the mordant solution afterwards, as for example, in Turkey-red dyeing.

Special methods of mordanting cotton are adopted occasionally, in accordance with the properties of the metallic salt employed. Stannic oxide, for example, may be fixed on cotton by passing the fabric through a solution of stannate of soda, and then through dilute sulphuric acid, and finally washing. Alumina is precipitated on the fibre by the mere exposure to air of cotton impregnated with aluminate of soda, in which case atmospheric carbonic acid is the active fixing-agent.

*b. The second important class of mordants is that which includes those of an acid character, and which are specially employed for fixing basic colouring matters on the vegetable fibres. The typical representative of this class is tannic acid.*

Cotton is mordanted with this substance by merely steeping in a cold solution of it, since it has a natural attraction for tannic acid; a subsequent passage through a hot or cold solution of a salt of antimony, tin, &c., serves to fix the tannic acid upon the fibre as insoluble metallic tannates.

Other acid mordants are the fatty acids, *e.g.* oleic acid, sulphated-oil, &c. With these the cotton is first impregnated, and they are fixed thereupon by passing through certain metallic salt solutions, *e.g.* aluminium acetate, previous to dyeing with the basic colouring matters.

Certain acid colouring matters derived from benzidine, fluorene, stilbene, &c., may also serve as acid mordants, since they, too, are naturally attracted by the cotton fibre, and they also produce insoluble compounds with basic colouring matters.

Even acid colouring principles may act as mordants towards those of a basic character. Alizarin, for example, when fixed on cotton by means of aluminium or iron, or even in the free state, readily attracts and combines with the colour-base of magenta, methyl-violet, &c., and the colour of the alizarin red or purple already on the cotton becomes modified or intensified.

**Basic mordants** are employed for fixing on animal and vegetable fibres those colouring matters which are of an acid character, *i.e.* either true acids or bodies containing hydroxyl groups, of which the hydrogen is replaceable by metals. They comprise the metallic salts, of which the most important are those of aluminium, iron, tin, and chromium.

The chief *aluminium mordants* employed for wool are aluminium sulphate and alum. The best results are usually obtained by merely boiling the wool for 1–1½ hours, in a solution containing 8–10 p.c. of the weight of the wool of aluminium salt, with the addition of cream of tartar, in the proportion of 3 mols. to 1 mol. aluminium sulphate. Aluminium tartrate also gives excellent results, but it is cheaper to allow this salt to be formed in the mordanting bath itself in the manner described. With some colouring matters oxalic acid and binoxalate of potash are to be preferred to cream of tartar as assistants.

Silk is mordanted by boiling with dilute aluminium sulphate solution, or by steeping 24 hours in a concentrated solution, and then washing in water, preferably calcareous.

The methods of mordanting cotton with aluminium are various. It may be impregnated with a more or less concentrated solution of alum or aluminium sulphate, dried, and then passed for a few minutes into a hot solution of phosphate, arsenate, or silicate of soda, or ammonium carbonate. The cotton may also be impregnated with a cold solution of neutralised sulphated oil, or of tannic acid, then dried and steeped in a solution of aluminium acetate or basic aluminium sulphate. One may also impregnate the cotton with a solution of aluminate of soda, dry, and expose to the air, or pass through a solution of ammonium chloride. Normal and basic aluminium acetates are also employed, the cotton being impregnated with their solutions, then dried, and exposed to a moist warm atmosphere ('ageing'), and finally passed through a hot solution of sodium arsenate &c. The aluminium acetates employed are prepared by dissolving alumina hydrate in acetic acid, or by decomposing a solution of aluminium sulphate with calcium or lead acetate ('red liquor'). As a general rule, the more basic the aluminium salts are, the more readily do their solutions precipitate by heating or diluting with water, and the larger is the quantity of alumina they yield to the fibre when used as mordants.

The chief *iron mordants* employed by the dyer are ferrous sulphate and acetate, ferric sulphate, acetate, and nitrate.



The ferrous acetate employed is made by dissolving scrap iron in pyroligneous acid. The 'pyrolignite of iron' or 'black iron liquor' thus obtained is preferable to that made by the mutual decomposition of ferrous sulphate and lead acetate solutions; it keeps better, being less liable to oxidise because of the presence of tarry matter or of reducing agents, *e.g.* pyrocatechol, &c. Ferric sulphate is prepared by heating a mixture of definite proportions of ferrous sulphate, sulphuric acid, and nitric acid. Although the last-mentioned substance is only used as an oxidising agent, the final preparation is generally termed by dyers 'nitrate of iron.' The so-called 'pure nitrate of iron' (ferric nitrate) is prepared by dissolving scrap iron in nitric acid.

Wool is not now very frequently mordanted with iron, except after the application of the colouring matter, *i.e.* by the so-called saddening method. In certain cases where it may be desirable to mordant with iron first in the ordinary manner, one may boil the wool in a solution of 7 p.c. ferric sulphate [ $\text{Fe}_2(\text{SO}_4)_3$ ] and 4 p.c. binoxalate of potash.

Silk is mordanted by merely steeping about twelve hours in a cold solution of pyrolignite of iron (sp.gr. 1.025), and afterwards washing well. The most usual mordant, employed largely in black silk dyeing, is the basic ferric sulphate  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{OH})_2$ . The silk is steeped in a somewhat concentrated solution of this salt (sp.gr. 1.25) for about one hour, then squeezed and well washed. The operations are repeated seven or eight times, after which the silk is boiled in an old soap bath and finally washed. In this process the very sensitive basic ferric sulphate absorbed by the fibre is decomposed during the several washings, a still more basic and insoluble salt being precipitated within the fibre.

Cotton is usually mordanted with iron by first impregnating it with cold tannic acid solution, and then, with or without drying, passing into a dilute solution of ferrous acetate, ferric sulphate or nitrate (sp.gr. 1.01-1.02). The cotton may also be impregnated with ferrous or ferric acetate, dried, and exposed to a moist warm atmosphere ('ageing'), and finally fixed by passing through a hot solution of sodium phosphate, &c.

*Tin mordants* are comparatively little used. As a rule the stannous salts are employed for wool and the stannic salts for cotton. The chief stannous mordant is stannous chloride or 'tin crystals.' It is frequently sold as a somewhat acid solution under the name of 'single muriate of tin' (sp.gr. 1.3), or of 'double muriate of tin' (sp.gr. 1.6). The general name 'tin spirits' is given to a variety of solutions of tin in mixtures of hydrochloric acid and sulphuric or nitric acid. They usually have a specific name according to the purpose for which they are employed; 'yellow spirit,' for example, is used in conjunction with the yellow dyewoods for dyeing yellows. A very favourite mordant with woollen dyers for producing cochineal scarlet is the so-called 'scarlet spirit' or 'bowl spirit.' It is really a stannous nitrate containing some stannic salt prepared by dissolving rods of block tin in cold nitric acid (sp.gr. 1.16) taking care to avoid too energetic action.

The chief stannic mordant employed is stannic chloride. It is usually sold as a solu-

tion, or the dyer makes it himself by dissolving tin in hydrochloric acid with the addition of some oxidising agent, *e.g.* nitric acid or potassium chlorate. The common name given to the solution is 'cotton spirits'; occasionally it receives such names as 'nitro-muriate of tin,' 'barwood spirits,' &c., according to its composition and character, and the use to which it is applied.

Wool is mordanted by boiling in a solution containing 6 p.c. of the weight of wool of stannous chloride, and 6-10 p.c. cream of tartar. Large proportions of stannous chloride should be strictly avoided, otherwise the dyed wool feels harsh and its general properties are impaired. Stannous chloride with addition of oxalic acid is particularly applicable for the single-bath process of dyeing with certain colouring matters, *e.g.* cochineal, flavin, alizarin, &c.

Silk may be mordanted in the same manner as wool, or it is steeped several hours in a more or less concentrated solution of stannic chloride and then well washed.

Cotton is mordanted with stannic oxide by impregnating it with a solution of stannate of soda (sp.gr. 1.02-1.05) and then passing rapidly through very dilute sulphuric acid and finally washing. The usual method, however, is to impregnate the cotton with cold tannic acid solution for three hours, then squeeze, and, with or usually without drying, steep one hour in a dilute solution of stannic chloride (sp.gr. 1.02), and wash. Cotton thus mordanted was much used formerly for dyeing with colouring matters of an acid character: peachwood, logwood, &c., in which case the stannic oxide constituted the mordant, the tannic acid acting as fixing-agent. Now that the basic coal-tar colours are so much employed in dyeing cotton, although the same method of mordanting is still employed, the rôles of the tin salt and tannic acid are reversed, for it is really the tannic acid which is the essential mordant while the stannic chloride serves only as the fixing agent.

The *chromium mordants* are now of the first importance, since with different colouring matters they yield a considerable range of colours which are remarkable for their permanence. The most important chromium salt is potassium bichromate, and it is now more largely used as a mordant in wool-dyeing than any other metallic salt. In cotton-dyeing it is frequently employed as an oxidising agent, *e.g.* to develop the colour in dyeing catechu-brown or aniline-black, and also to dye chrome of lead yellow and orange. In recent years the cheaper sodium bichromate has largely replaced the potassium salt. Other chromium salts employed as mordants, chiefly for cotton, are chrome-alum and chromium acetate. Chrome-alum is obtained in large quantities as a by-product during the manufacture of alizarin; chromium acetate is prepared by mixing together solutions of chrome-alum and lead acetate.

Wool is mordanted with chromium by boiling for 1-1½ hours with 3 p.c. (3 mols.) potassium bichromate. In many cases it is beneficial to add along with it 1 p.c. (1 mol.) sulphuric acid (sp.gr. 1.84) or 6 p.c. (1 mol.) tartaric acid, whereby fuller or brighter colours are ultimately obtained. When potassium bichromate alone is employed it would appear that a decomposition of the salt

occurs, the wool absorbing essentially chromic acid as well as potassium bichromate. When an addition of sulphuric acid is made the wool absorbs only chromic acid. In both cases the mordanted wool has a yellow colour, and only in the dye-bath does the reduction to the real mordanting body chromic oxide take place within the fibre through the interaction of the colouring matter. When tartaric acid is the assistant employed the mordanted wool has a green colour, reduction of the chromic acid taking place already in the mordanting bath, and chromic hydrate being deposited within the wool. If large amounts of potassium bichromate are employed for mordanting, especially if sulphuric acid is also added to the bath, bad results are obtained, the colouring matter being oxidised and destroyed by the excess of chromic acid present in the wool. This defect is known as 'over-chroming.' In some few cases potassium bichromate may be usefully applied in the same bath with the colouring matter, *e.g.* with alizarin, or after it, *e.g.* in the case of camwood.

Silk is not usually mordanted with chromium. It is well mordanted, however, if boiled with a solution of potassium bichromate and tartaric acid after the manner of wool, but not if one employs potassium bichromate alone, or even with the addition of sulphuric acid.

Cotton is mordanted with chromium by impregnating it with a more or less concentrated solution of chrome-alum, drying, and passing through a boiling solution of sodium carbonate (100 grams per litre) or caustic soda. A method in vogue with the printer is, to impregnate or print the cotton with a mixture of colouring matter and chromium acetate, dry and steam ('steam colours'). Cotton may also be mordanted by steeping for several hours in an alkaline solution of chromium acetate, *e.g.* a mixture of 100 parts by weight of chromium acetate (sp.gr. 1.115), 100 parts NaOH (sp.gr. 1.33), 50 parts water, and finally washing. This method, however, is not employed, it is found better to pad in the solution and steam.

**Acid mordants** are employed for fixing basic colouring matters on cotton. They find no use for this purpose in wool and silk dyeing, since these fibres themselves act as acid mordants, and are dyed directly without the aid of any mordant.

**Tannic acid** is the mordant *par excellence* for fixing the basic coal-tar colours on cotton. This fibre absorbs tannic acid by long steeping in its cold solution, and if when thus prepared it is immersed in a solution of a basic colouring matter, the tannic acid combines with the colour-base, a coloured lake is formed within the substance of the fibre and the cotton becomes dyed. During the dyeing process the acid originally in combination with the colour-base is displaced, and since in the free state it interferes with the complete formation of the colour-lake, it is found beneficial to add a small proportion of sodium carbonate or acetate to the dye-bath. Since the tannates of colour-bases are somewhat soluble, especially if there be excess of tannic acid present, and also in alkaline solutions, it is necessary in practice to fix the tannic acid on the fibre in the form of an insoluble metallic-tannate, previous to dyeing. This is done by passing the tannic acid prepared cotton through

a hot or cold solution of tartar-emetic or stannic chloride; tannate of antimony or tin is thus fixed on the fibre, and these have quite as great an attraction for the colour-base as free tannic acid has. Cotton thus mordanted and dyed is probably permeated with a very insoluble tannate of antimony or tin and of colour-base, a triple compound which is insoluble in alkaline solutions, and fast therefore to washing with soap, &c.

As already pointed out, tannic acid is sometimes used as a *fixing agent* for tin, iron, or aluminium mordants, and since its iron compound is of a bluish-black colour it sometimes serves with respect to iron as a useful *colouring matter*.

Tannic acid finds no use in woollen dyeing, but for silk it is largely employed, partly for adding weight to the silk, and partly for the purpose of dyeing it black in conjunction with iron mordants. Its utility as a weighting agent is owing to the fact that silk absorbs as much as 25 p.c. tannic acid from its hot solution, whereby it not only gains in weight, but also in volume.

**Fatty acids** are used as mordants for fixing the basic coal-tar colours on cotton very much in the same way as tannic acid. They are, however, not attracted by cotton from their solutions, but they form insoluble lakes with the colour-bases. The method of procedure is to impregnate the cotton with a more or less concentrated solution of their alkali salts, *e.g.* soap; after drying, the fabric is passed through, or better steeped, in a cold solution of aluminium sulphate, and washed. Although the fatty acid is thus fixed on the fibre as an insoluble aluminium-soap, it is still capable of combining with the colour-base when the cotton is passed into a solution of a basic colouring matter. Colours dyed by this method are brighter than, but not so fast to washing as, those fixed by means of tannic acid.

The most convenient fatty-acid mordant to employ instead of ordinary soap is the so-called 'sulphated-oil.' It is prepared by mixing two parts by weight of castor-oil with one part of sulphuric acid (sp.gr. 1.84) and allowing the mixture to stand for 24 hours. It is then washed with a strong solution of common salt to free it from excess of acid, and is finally neutralised with ammonia or caustic soda. The product of the action of the acid upon the oil has a somewhat complex chemical composition, but its practical utility depends upon the fact that it behaves like a fatty acid and gives an extremely soluble soap with alkalis. Ordinary castor-oil soap produced by boiling the oil with caustic soda is also very soluble and may be used as an equally good mordant. Sulphated-oil is frequently called 'Turkey-red oil,' 'alizarin-oil,' and 'soluble-oil,' since it is largely used in the modern short process of Turkey-red dyeing as the fixing-agent for the necessary aluminium mordant, and it gives the characteristic brilliancy of colour obtained by the use of the oil preparations formerly employed.

Acid colouring principles, *e.g.* alizarin, and certain acid colouring matters derived from benzidine, stilbene, fluorene, &c., can also be readily fixed on cotton, and serve as mordants for basic colouring matters, but they are not generally



used for this purpose unless for the production of compound shades to suit certain tastes or requirements.

**Natural colouring matters.** These belong for the most part to the acid or phenolic class, and require therefore the aid of basic mordants (metallic salts). The notable exceptions are indigo, safflower, turmeric, catechu, annatto, and arcilal.

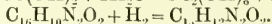
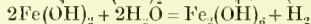
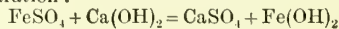
*Indigo* is one of the most valuable blue colouring matters employed by the dyer.

One method of dyeing with indigo is founded upon its property of dissolving in strong sulphuric acid whereby it becomes changed into indigotin-disulphonic acid (indigo-extract), which is then applied to the animal fibres by merely steeping them in its hot acid solutions. This method, which is not applicable to the vegetable fibres, yields brighter colours than the vat-method described below, but they are fugitive to light and are decolourised by alkaline solutions.

The most important method of application is by means of the indigo-vat, which is suitable both for vegetable and animal fibres and yields exceedingly permanent colours although they are not remarkable for brilliancy. This method is based upon the fact that under the influence of reducing agents, the insoluble indigo-blue is changed into indigo-white which is readily soluble in alkalis. If textile materials are immersed in the alkaline solutions and then exposed to the air, the indigo-white absorbed by the fibre is oxidised and reconverted into indigo-blue, which being precipitated within and upon the fibre is permanently fixed.

Cotton is dyed by means of the ferrous sulphate vat, the zinc-powder vat, or the hyposulphite vat.

The *ferrous sulphate vat* (lime and copperas vat) is composed of the following ingredients: water 4,000 litres, finely ground indigo 40 kilos., ferrous sulphate 60-80 kilos., dry slaked lime 50-100 kilos. The following equation shows the chemical changes which occur during its preparation:

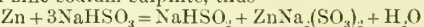


The lime decomposes the ferrous sulphate with the production of ferrous hydrate, and this in the presence of lime and indigo decomposes the water, yielding ferric hydrate and hydrogen; the latter at once combines with the indigotin and produces indigo-white, which dissolves by reason of the excess of lime present. The normal colour of the vat liquor thus obtained is brownish-amber.

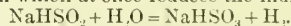
The *zinc-powder vat* is made up with water, indigo, zinc-powder, and lime. In the presence of the lime and indigo the zinc decomposes the water even at the ordinary temperature, and the liberated hydrogen effects the reduction of the indigo.

The *hyposulphite vat* contains water, indigo, hyposulphite of soda ( $\text{NaHSO}_3$ ) and lime. The active reducing agent hyposulphurous acid (also called hydrosulphurous acid) is prepared by the short action (1 hour) of zinc-powder upon a cold concentrated solution of bisulphite of soda (sp.gr. 1.3), taking care to avoid access of air and over-

heating of the mixture. After neutralising with lime and allowing the sediment produced to subside, the clear solution of hyposulphite is mixed with lime and indigo. The action of the zinc upon the bisulphite of soda is somewhat complex, there being produced a solution of sodium hydrogen hyposulphite and a precipitate of zinc sodium sulphite, thus—



In the presence of the indigo and lime the sodium hydrogen hyposulphite decomposes the water, yielding sodium hydrogen sulphite and hydrogen which at once reduces the indigo;



The advantages of this vat are, that it is readily prepared and gives very little sediment.

Wool is also dyed by means of the hyposulphite vat, but more frequently the fermentation vats are employed, of which the principal is the so-called woad-vat. The composition of this vat is about as follows:—

Indigo 15 kilos., woad 300 kilos., bran 10 kilos., madder 2-15 kilos., lime 12 kilos., water 6,000 litres. The bran, madder, and especially the woad, supply the ferment, a species of bacterium which at a temperature of about 50°C. causes lactic and butyric fermentation with evolution of hydrogen. Excessive fermentation is prevented by making suitable additions of lime, or it is accelerated, if necessary, by adding further quantities of bran.

In the so-called German soda-vat and the Indian potash-vat, the woad is replaced by bran with the addition of molasses, and the lime is more or less replaced by sodium or potassium carbonate.

To avoid the derangements to which all fermentation vats are liable, Collin and Benoist propose to employ a pure ferment and a completely fermentescible food material. The latter consists of starch paste and glucose, while the former, *Desmobacterium hydrogeniferum* is cultivated by infecting a sterilised solution containing sodium carbonate and phosphate, ammonium tartrate, soluble starch and lime, with a crude ferment obtained by digesting potato cuttings in tepid water. It is proposed to sell the pure ferment mixed with dry wood-flour, of which preparation 50 grams would suffice for a vat of 12 cubic metres capacity. The results obtained by its use are said to be 40 p.c. better than those of the old method.

Silk is seldom dyed with vat blue. Both the fermentation and the hyposulphite vat are applicable, or one may employ with advantage a vat prepared with zinc-powder and ammonia.

*Logwood* serves principally for producing blacks, dark blues, greys, and numerous compound shades when used along with other dye-stuffs.

Wool is dyed blue or black by mordanting with bichromate of potash, with the addition of sulphuric or tartaric acid, or cream of tartar, then washing and dyeing in a separate bath with 15-50 p.c. logwood. It is usual to modify the tone of colour by the addition of a small quantity of some other dyewood—e.g. fustic. When sulphuric acid is the assistant employed in the mordanting bath, or if no addition is made, the presence of chalk or calcium acetate in the dye-bath is injurious, whereas if tartaric acid or



cream of tartar is employed, these additions are decidedly beneficial. Occasionally wool is dyed black by mordanting it with ferrous sulphate before or after dyeing with logwood. A direct black, known as 'Bonsor's Black,' is a mixed iron and copper lake sold in the form of a paste. Wool is dyed by boiling with a solution containing 20-30 p.c. of the paste, and 2-3 p.c. oxalic acid. Woaded blacks are produced by first dyeing a light indigo blue in the woad-vat and then dyeing logwood black in the ordinary manner. With aluminium mordant logwood gives a dull purple, and with tin mordant a still redder purple, both fugitive to light. In the former case the presence of chalk or calcium acetate in the dye-bath is beneficial. With copper mordant it yields a greenish-black remarkable for its fastness to light. These mordants are employed much less frequently than bichromate of potash.

Silk is dyed black as follows:—Mordant with basic ferric sulphate, dye blue in a bath of potassium ferrocyanide slightly acidified with hydrochloric acid, steep in a strong hot decoction of catechu containing stannous chloride, steep in a second bath containing only catechu, mordant with pyrolignite of iron, dye in a bath containing logwood liquor and soap.

Cotton is dyed black by first preparing it with tannic acid (decoction of myrobalans, sumach, &c.) or with catechol (decoction of catechu), then mordanting with pyrolignite or nitrate of iron, and finally dyeing with logwood. Aluminium, tin, and copper mordants are only occasionally employed in connection with logwood by the cotton dyer.

*Brazilwood*, *peachwood*, and *limawood* possess dyeing properties more or less similar, and the method of their application to the different fibres is practically the same as for logwood. They are becoming less and less employed because of the fugitive character of the colours they yield.

With chromium mordant they produce colours ranging from purplish-slate to claret-brown, according to the percentage of dyewood employed. With aluminium and tin mordants they give moderately bright crimsons, with copper and iron mordants claret-brown and dark slate respectively.

In the form of extracts these dyewoods are still much used by the calico-printer for low class steam styles.

*Cannwood*, *barwood*, and *sanderswood* possess similar dyeing properties, and are chiefly employed in woollen-dyeing for producing brown colours. The colouring matter which they contain is of a resinous character and very little soluble even in hot water; but if wool is boiled with water containing the ground wood it absorbs a considerable quantity of colouring matter and acquires a full reddish-brown stain. By passing afterwards into boiling solutions of the various mordants useful colours are obtained. Chromium mordant gives a deep purplish-brown, aluminium a brownish-red, copper and iron mordants a claret-brown and purplish-brown respectively. With these dyewoods this so-called 'stuffing and saddening' method of dyeing is preferable, as a rule, to the ordinary 'mordanting and dyeing' method, since it gives deeper colours.

In cotton-dyeing barwood is the only dyestuff of this class used, viz., for 'mock Turkey-red' or 'barwood red.' The cotton is prepared with tannic acid, mordanted with tin, and boiled with water containing ground barwood.

In silk-dyeing these dyewoods are never employed, because the addition of ground wood to the dye-bath is inadmissible with silk, and no extracts are obtainable.

*Madder*. This dyestuff, once of such great importance, has now been almost entirely replaced by artificial alizarin, particularly in cotton-dyeing.

Wool is mordanted with bichromate of potash, aluminium sulphate, &c., according to the methods already described, and dyed in a separate bath with madder. The addition to the dye-bath of 1-2 p.c. of chalk or calcium acetate is beneficial, especially in the case of aluminium and iron mordants, or when chromium is present in the wool as chromic hydrate. Chromium gives claret-brown, aluminium brownish-red, tin gives a fairly bright orange, copper and iron mordants give brown. With stannous chloride and oxalic acid, also with potassium bichromate and sulphuric acid, the 'single bath' method of dyeing may be employed.

Silk is mordanted in the usual manner and dyed in a separate bath with madder.

The use of madder in the woad-vat has already been referred to.

*Cochineal*. This valuable dyestuff is principally used in wool-dyeing for the production of crimson and scarlet colours, although it is now largely replaced either by azo-scarlet or alizarin-red. In cotton and silk dyeing its use is all but entirely discontinued.

Wool is dyed crimson by first mordanting with aluminium sulphate and cream of tartar, and dyeing in a separate bath with cochineal. By employing oxalic acid as the assistant the single-bath method may also be employed. Cochineal scarlet is always dyed in a single bath, using about 6 p.c. stannous chloride, 6 p.c. oxalic acid, and 10-15 p.c. ground cochineal; usually a small percentage of flavin is added to make the colour yellower and brighter.

Chromium and iron mordants give purple and slate colours respectively; but these mordants are rarely employed in practice, because similar colours can be obtained more cheaply by other methods. The presence of lime salts or any alkaline salt in the dye-bath is specially injurious. All cochineal colours are fast to light; the chief defect of cochineal scarlet is that it loses brilliancy and becomes blue by the action of alkalis, soap, &c.

*Lac-dye* may be employed in the same way as cochineal, and similar colours are obtained with the different mordants; but its use is now almost entirely discontinued. Owing to the presence of an excess of mineral matter in lac-dye it is necessary to soak it in a little dilute hydrochloric acid before use.

*Archil*, in the form of paste or extract, or in the dried state as *cudbear*, is employed in wool and silk dyeing for the production of compound colours—chiefly browns, maroons, olives, &c. It is applied in a neutral, slightly alkaline, or slightly acid bath. It yields full rich colours, which unfortunately are not fast to light.

*Annatto* is now little used, except in silk-dyeing. It is applied in a hot soap bath. It gives nice orange shades, which are fugitive with respect to light.

*Safflower* was formerly much used for dyeing bright pinks on cotton; but its employment for this purpose is now almost entirely discontinued. Cotton is dyed in a slightly alkaline bath, which is gradually acidified by the addition of tartaric, acetic, or sulphuric acid, the colouring matter being thus precipitated upon the fibre.

*Weld* is now employed only to a limited extent in silk and wool-dyeing, chiefly for producing yellow in conjunction with tin and aluminium mordants, or for olive with iron mordant.

Wool is dyed yellow by mordanting with 4 p.c. aluminium sulphate with the addition of cream of tartar, and dyeing in a separate bath with 80 p.c. weld, with the addition of 8 p.c. chalk. Silk is dyed in a similar manner. The colour is remarkable for its purity, i.e. freedom from orange, and its fastness to light. With tin mordant a pure, bright, and fairly fast yellow is also obtained.

*Old-fustic* is the most largely used natural yellow dyewood now employed, principally in wool-dyeing, for the production of compound shades. With chromium mordant it yields an olive-yellow (old-gold) colour, with aluminium and tin mordants yellows are obtained, those with tin being the brightest; copper and iron mordants give olives. Prolonged dyeing, especially at high temperatures, should be avoided in the case of yellows, otherwise the colours become dull. The brightest yellows are those obtained with tin mordant in single bath. The chromium and iron colours are fast to light.

*Quercitron-bark* is not much used in dyeing, except by the calico-printer, because of its comparatively high price. With the different mordants it gives shades more or less similar to those yielded by old-fustic; the yellows produced by the aid of tin mordant are brighter and more orange.

*Flavin*, which consists essentially of quercetin, the modified colouring of quercitron-bark, is almost entirely used in wool-dyeing, and chiefly for bright orange or yellow in conjunction with tin mordant by the single-bath process. It is used along with cochineal to obtain yellow shades of scarlet.

*Young-fustic* yields fugitive colours; hence it is gradually falling into disuse. On wool mordanted with bichromate of potash it gives a reddish-brown, with tin mordant a bright orange-yellow, very similar to that given by quercitron bark and flavin.

*Persian-berries*. This dyestuff is chiefly used by the calico-printer, since it is much more expensive than other yellow colouring matters, which serve the purpose of the dyer equally well. With the different mordants it yields colours similar to those given by other yellow dyewoods. On wool it produces a good reddish-brown with chromium mordant, and with tin mordant a particularly bright orange. The olive colour obtained by means of copper mordant is remarkable for its fastness to light.

*Turneric* is still largely used in wool, silk, and cotton-dyeing, because of its cheapness, notwithstanding the very fugitive character of the

colour it yields. Wool and silk may be dyed yellow without making any addition to the dye-bath, but brighter colours are obtained by acidifying the bath with aluminium sulphate.

Cotton is dyed simply by immersion in a hot decoction of turmeric, without having been previously mordanted. The yellow colour thus obtained is fugitive to light, and is changed to reddish-brown by alkalis.

*Catechu* is a most valuable dyestuff, and is largely used in cotton and silk-dyeing. In wool-dyeing it finds little or no employment.

In silk-dyeing it is used to add weight to logwood blacks. After mordanting with basic ferric sulphate and dyeing Prussian blue, the silk is steeped in a hot and strong decoction of catechu with or without the addition of stannous chloride. The silk absorbs a very large percentage of catechol, which is fixed on the fibre as a tin-lake. Mordanting with pyrolignite of iron and dyeing with logwood follow the weighting operation.

Dark browns are produced on silk plush intended to imitate seal-skin, by working the silk in a hot catechu decoction, and afterwards passing into a solution of bichromate of potash.

Cotton is dyed brown in the manner just described for silk. In both cases the catechol absorbed by the fibre is oxidised and changed into a brown insoluble substance called japonic acid. Dark shades are best dyed by repeating the processes. Catechu may be used instead of tannic acid for fixing iron mordant previous to dyeing logwood black, or as a mordant for basic coal-tar colours. Catechu browns, especially on cotton, are extremely fast to light and most other agencies.

**Artificial colouring matters.** This group includes every variety of colouring matter, basic, acid, and neutral, and their methods of application are very varied, although they are in some measure always dependent upon the chemical constitution of the individual colouring matters.

**Nitro-colouring matters.** The important members of this class are: picric acid, Victoria orange, aurantia, palatine orange, naphthaliu yellow, naphthol yellow S. All these colouring matters are only applicable to the animal fibres, which are dyed in a bath slightly acidified with sulphuric acid. The colours they yield are not fast to light. Picric acid yellow is remarkable for its extreme freedom from any trace of orange. On exposure to light it rapidly becomes orange, and then gradually fades.

**Azoxy-colouring matters.** The sole representative of this class is Curcumin S,  

$$C_{17}H_{14}(N_2O)(NaSO_3)_2$$

It is applied in exactly the same way as the nitro-colouring matters.

**Nitroso-colouring matters.** This class includes fast-green or dark-green and naphthol-green B. In conjunction with iron mordants both these dyestuffs give olive-green colours remarkable for their fastness to light.

Cotton is dyed with dark-green by mordanting with iron and dyeing in a neutral bath. Wool is mordanted with ferrous sulphate and oxalic acid, and dyed in a neutral bath. Silk is dyed in a similar manner.

Naphthol-green is only applicable to the animal fibres. Wool is dyed in a single bath



with the addition of ferrous sulphate and sulphuric acid.

*Azo-colouring matters.* This large group comprises several sub-divisions: amido-azo-colours, oxy-azo-colours, benzidine colours, &c.

The chief amido-azo-colours are aniline yellow, chrysoidine, Bismarck brown. Of these only the two last are now used, the first-named being too fugitive and sensitive. Cotton is mordanted with tannic acid and tartar emetic, and dyed in a neutral bath. Wool and silk are dyed in a neutral bath. None of the colours produced are fast to light. Of the amido-azo-sulphonie-acid colours the following may be mentioned: Fast yellow, dimethylaniline orange, or orange III., diphenylamine orange or orange IV., metanil yellow, brilliant yellow, and azo-flavin. These colours are not suitable for cotton. Wool and silk are dyed with the addition of sulphuric acid. The colours are only moderately fast to light.

The oxy-azo-colours are exceedingly numerous, and include yellow, orange, red, brown, and black or dark-blue colouring matters. They are for the most part sulphonic acid colours, and are hence specially applicable to wool and silk, which are dyed in an acid bath. Although many yield colours having only a moderate degree of fastness to light, others are very good indeed in this respect, e.g. the tetrazo-compounds, such as erocin scarlet, &c. The following are a few of the leading colours of this class: Chrysoin, orange I., orange II., orange G, Ponceau R, Biebrich scarlet, erocin scarlet, fast red, archil brown, Bordeaux, amaranth, naphthol black, wool black, &c.

Of these colours the oranges and reds present little or no difficulty in dyeing if the temperature of the dye-bath is raised very slowly to the boiling-point, but the browns, Bordeaux, and dark blues are exceedingly apt to dye uneven shades, the colour being for the most part precipitated on the surface of the wool or silk. To prevent this it is well to add to the dye-bath 5-10 p.e. on the weight of wool, of sodium sulphate. Azarin S differs somewhat in constitution from the foregoing. It is a non-sulphonated azo-red, which has been rendered soluble by means of bisulphite of soda. It is specially suitable for cotton, which is first mordanted with aluminium, and dyed with the addition of sulphated-oil.

An interesting method of dyeing cotton with the azo-colours consists in immersing the cotton alternately in solutions of an azo-compound (e.g. diazo-benzene chloride) and of a phenol. It is best to apply the phenol solution first, and dry the fabric before passing into the azo-solution. The azo-colour is precipitated upon the fibre, and, although fairly fast to light and washing, it tends to rub off.

The benzidine and allied colouring matters seem likely to become as numerous as the oxy-azo-colours. Their distinguishing feature, to which they owe their great utility, is that they dye cotton direct, in a neutral or slightly alkaline bath. The addition of a certain proportion of common salt is essential, since it gives deeper colours, probably because it tends to precipitate the colouring matter upon the fibre.

The following are a few of the colours of this class: Congo red, benzopurpurin, azo-blue, benzo-azurin, chrysanin, Hessian yellow, &c.

Primulin is the representative of a special class of amido-colouring matters (containing sulphur) which dye cotton directly. It dyes cotton in a neutral bath a bright yellow colour. If the dyed colour is azotised by passing the fabric through a solution of nitrous acid, a variety of colours, e.g. orange, red, brown, and blue, can be developed from it by further passing through alkaline solutions of various phenols and amines. The colours are fast to soap, but not to light.

Tartrazin is a yellow azo-colour of special constitution derived from phenyl-hydrazin, but, being a sulphonic acid compound, it is applied to wool and silk in the usual manner, and is not applicable to cotton. It is specially remarkable for yielding colours which are extremely fast to light. It is indeed the fastest to light of all yellows now known.

*Triphenylmethane colours.* This class includes the most important basic colouring matters, a few sulphonic acids of colour-bases, and one or two hydroxyl compounds of little importance to the dyer.

The basic colouring matters comprise the following: Magenta, rosaniline blue or spirit-blue, rosaniline violet, Hofmann's violet, methyl violet, methyl green, benzaldehyde green, ethyl purple, crystal-violet, Victoria blue, night-blue, auramine.

Wool is dyed with most of these colours in a neutral bath, heating gradually up to the boiling-point. The addition of sodium acetate in small quantity is beneficial, since it changes the chlorides of the colour-bases into the acetates. Silk is dyed in a neutral bath with the addition of boiled-off liquor, i.e. waste soap-liquor containing silk-glue. The exceptions to the above rule are rosaniline blue and violet, which require a slight addition of sulphuric acid to the bath; Victoria blue and night-blue require either the same addition or a little acetic acid instead, in order to prevent precipitation of the colouring matter in the dye-bath.

Cotton is mordanted with tannic acid and tartar emetic and dyed in a neutral bath.

The sulphonic acid colours of this group include the following: acid-magenta, acid-violet, acid-green. All these are specially suitable for wool and silk-dyeing and are inapplicable to cotton, the former being dyed with the addition of sulphuric acid to the bath. Soluble-blue is also an acid colour, but it dyes tannin prepared cotton fairly well if the bath is acidulated with alum.

Alkali blue, green, and violet are also sulphonic acid colours specially suitable for dyeing wool, to which they are applied in a special manner. The wool is boiled with a solution of the alkali salt of the colour-acid, for which it seems to possess a definite attraction. The fabric, which at this stage has only a pale tint, is then passed into warm dilute sulphuric acid, whereby the colour-acid is liberated within the fibre which thus becomes dyed, a full colour being developed.

Of the hydroxyl derivatives of triphenylmethane only aurine has acquired any importance, but it is not now used in dyeing because of its extremely fugitive character. None of the triphenylmethane derivatives appear to be fast to light. Wool dyed with most of them is not suitable



for goods which have to be milled, since the colour 'bleeds'; notable exceptions are Victoria blue and night-blue. Fixed on cotton they withstand the action of soap remarkably well.

**Phthalein colouring matters.** These include two classes of hydroxyl derivatives. The members of the first class comprise eosin, erythrosin, rose-bengale, phloxin, cyanosin. They are specially suitable for wool and silk, these fibres being dyed in an acid bath. Cotton impregnated with lead acetate and dried may also be dyed in neutral solutions, a lead-lake being formed upon the fibre. All the above colours are remarkable for the brilliancy of the dyes they yield, but which, unfortunately, are among the most fugitive.

Rhodamine is a brilliant pink amido-colouring matter related to the foregoing and remarkably fast to light. It is a basic colouring matter, and applied according to the method usual for this class of dyestuffs.

The second class of phthalein colours includes the two important dyestuffs gallein and cœrulein. Unlike the foregoing colours they only yield useful dyes when applied in conjunction with mordants which must of necessity have a basic character.

Wool, silk, and cotton are mordanted according to the usual methods with metallic salts, and dyed in a separate bath with the colouring matters.

Gallein yields with chromium mordant a bluish-purple colour, with aluminium a reddish purple, with iron mordant a deep-violet colour. The chromium mordant is the most useful, especially in the case of wool. All the colours are fairly fast to light.

Cœrulein yields with the different mordants various shades of olive-green, all of which are remarkably fast to light. In wool-dyeing the chromium mordant is the most useful. Cœrulein S is the soluble sodium bisulphite compound of ordinary insoluble cœrulein. It is applied in the same manner, care being taken to dye for some time at a temperature of 50°–60°C., since at a higher temperature it is decomposed, the ordinary insoluble cœrulein being liberated. Attention to this point ensures more level shades. The presence of lime salts in the dye bath is injurious. Gallein and cœrulein are very useful colouring matters to apply along with anthracene colours in order to obtain compound shades of fast brown, olive, &c.

**Anthracene colouring matters.** This is one of the most important classes of dyestuffs, because it comprises those which give colours remarkable for their fastness to light and other agencies. The colouring matters at present in use are alizarin, anthrapurpurin, flavopurpurin, purpurin, nitro-alizarin or alizarin orange, alizarin blue, anthragallol or anthracene brown. All these, being phenolic colouring matters, require the aid of basic mordants.

The various fibres, wool, silk, and cotton are mordanted in the usual manner with metallic salts, and then dyed in separate baths with the colouring matters.

*Alizarin, anthrapurpurin, and flavopurpurin*, give similar shades with the different mordants, viz., brown with chromium, red with aluminium, orange with tin, purple or slate with iron mordants.

In wool-dyeing the chief mordants employed are bichromate of potash, and aluminium sulphate with addition of cream of tartar. With the former the presence of lime salts in the dye bath is not necessary, but with the latter it is all-essential, the best form being calcium acetate. The coloured lake fixed upon the fibre is an aluminium-calcium compound of the colouring matter. The usual form of alizarin, anthrapurpurin, and flavopurpurin is that of thin watery pastes containing 20 p.c. of solid matter, but they also occur in the form of powder under the name of alizarin S, 2S, 3S, WS, &c. These are sulphonic acids of the ordinary products, and are specially useful in wool-dyeing because they are more soluble and yield more readily level colours. Their method of application is exactly the same. With the chromium, aluminium, tin, and iron mordants useful single-bath methods are available.

In silk-dyeing the fibre is mordanted as usual, and dyed in a separate bath as in wool-dyeing.

In cotton-dyeing these colouring matters are chiefly used for the production of Turkey-red, the essential feature of which is that it possesses a remarkable brilliancy and fastness—because of the presence on the fibre of oil in a modified insoluble form in conjunction with the alizarin and aluminium mordant.

The preparation of the fibre with olive oil is effected, according to 'Steiner's process,' by passing the fabric once through hot oil and then several times through weak solutions of alkaline carbonate, exposing the material between each passage to a temperature of 70°C. in a stove. After removing unchanged oil by means of warm dilute carbonate of soda, the cotton is mordanted in a slightly basic solution of aluminium sulphate or acetate, washed and dyed with alizarin. After dyeing, the colour is rendered brighter by boiling under pressure with soap to which a little stannous chloride may be added. This process is only suitable for cloth.

The so-called 'emulsion process' employed for cotton yarn differs from the above, mainly in that the material is not passed through hot oil, but receives repeated immersions in emulsions composed of olive oil and carbonate of soda or potash, being exposed after each immersion to 70°C. in a stove.

Both these processes seem to be gradually giving way to the much shorter 'sulphated-oil process,' in which the cotton is impregnated with an alkaline solution of sulphated castor oil or olive oil and then dried. Thus prepared it is mordanted with basic aluminium sulphate or acetate, dyed, dried, steamed, and boiled with soap solution. The steaming operation after dyeing helps materially to brighten and fix the colour-lake upon the fibre.

In all these processes the oil, in the form of a modified fatty acid, acts the part of a fixing-agent for the alumina, and enters into the composition of the red lake, imparting to it both brilliancy and permanency.

*Nitro-alizarin* is applied to the various fibres in exactly the same way as alizarin. Its chief employment is in wool-dyeing, with bichromate of potash as the mordant, for the production of compound shades. It gives a reddish-brown, very

similar in shade to that given by madder. With aluminium and tin mordants it gives an orange colour, with copper a brownish-red, and with iron a purplish-brown.

*Alizarin blue* occurs either in an insoluble form as a dark blue almost black paste, or in a soluble form as a reddish-brown paste. The latter, known as alizarin blue S, is the sodium bisulphite compound of the former. Both forms are used principally in wool-dyeing, the material being mordanted with bichromate of potash. With alizarin blue S care must be taken to dye for some time at 50°–60°C., since above this temperature the compound decomposes, yielding the insoluble form which does not penetrate the fibre so well. Calcareous water is not beneficial, and the dye bath should always be acidified slightly with acetic acid. All the metallic mordants give various shades of blue, that yielded by chromium is a rich purplish-blue. When used in combination with *cœrulein*, nitro-alizarin, &c., very deep-blue shades may be obtained very similar to those yielded by vat-indigo, for which alizarin blue seems likely to become a serious rival. It yields colours fast to light, milling, and all natural agencies.

Satisfactory results may be obtained also in silk and cotton-dyeing by adopting the usual methods of mordanting and dyeing in separate bath.

*Anthragallol* or *anthracene brown* is principally used in wool-dyeing, and with bichromate of potash mordant gives dark-brown shades remarkable for fastness to light and other agencies. It is applied in the same manner as alizarin.

*Naphthazarin*, the alizarin of naphthalene, is now employed as a sodium bisulphite compound in wool-dyeing under the name of *alizarin black*. It is applied in the same manner as alizarin blue S, and with chromium mordant yields a somewhat brownish-black, very fast to light and other agencies. Its chief use is for the production of compound shades.

*Galloflavin*, although not an anthracene colour, is best mentioned here because it is applied in the same manner as the foregoing. It is prepared by oxidising an alkaline solution of gallic acid at a low temperature, and is sold as a yellowish paste. In wool-dyeing, where it is chiefly employed for compound shades, it gives with the various mordants colours very similar to those given by old-fustic.

**Quinoline and acridine colouring matters.** The members of this group are—flavaniline, quinoline red, quinoline blue, alizarine blue, chrysaniline or phosphine, and quinoline yellow. Of these only the last three are now of any practical importance.

*Alizarin blue* has already been spoken of as an anthracene colour.

*Phosphine*, being the hydrochloride of a colour-base, is a basic colouring matter, and is applied in exactly the same manner as magenta. It yields a dull orange colour not remarkable for any special feature. Being very expensive it is now very little used.

*Quinoline yellow* is the sodium sulphate of quinophthalin and, as such, is applicable only to the animal fibres in an acid bath. It dyes wool and silk a pure yellow colour exactly

similar to that given by picric acid, but which possesses the advantage of greater fastness to light.

**Indamine and indophenol colouring matters.** To this group belong Bindschedler's green, toluylene blue, and indophenol blue. Of these, only the last-mentioned has been employed in practice for dyeing. Formerly the calico and woollen printer obtained indigo-blue shades by printing on the fabric a tin-reduction compound (indophenol-white), steaming and developing the colour by passing through a solution of bichromate of potash. The colour was very sensitive to acids, whereby it was changed at once to a reddish brown. Indophenol blue is now used along with indigo for dyeing cotton, employing a hyposulphite vat containing stannous chloride.

**Thionine colouring matters.** *Methylene blue* is an important colouring matter of this group. It is of a basic character, and consequently applied to the various fibres in exactly the same manner as magenta. It is only used in cotton-dyeing for dark indigo-blue shades, for which purpose the fibre is mordanted with tannic acid and nitrate or acetate of iron.

**Oxazine colouring matters.** *Gallocyanin* or *Fast violet*, is a useful dye-stuff which dyes wool and silk direct, but being of a phenolic character it may also be fixed on these and also vegetable fibres by means of mordants, when it yields more permanent colours. It yields various tones of purple with the different mordants, of which chromium is the most useful.

*Prune* is closely allied to gallocyanin, and is similarly applied.

*Meldola's blue* or *New blue*, and *Muscavin*, are allied dark-blue colouring matters specially applicable to cotton prepared with tannic acid and tartar-emetic. The former is very fast to light.

*Nile blue* is a bright blue amido-colouring matter of this class suitable for cotton and applied in the same manner as Meldola's blue. It is not fast to light.

**Azine, eurhodine, and saffranine colouring matters.** This group comprises the following commercially useful colouring matters—neutral red, or toluylene red, neutral blue, neutral violet, and saffranine. All these are basic colouring matters, and are applied to the various fibres according to the methods suitable for this class. They are chiefly employed in cotton-dyeing. When fixed on cotton with tannic acid and tartar-emetic they are fast to soap, and also tolerably fast to light, at least very much more so than the basic colouring matters of the triphenylmethane group.

Closely related to the foregoing is *Magdalarad*, an expensive colouring matter, now only occasionally employed in silk-dyeing for producing certain delicate shades of pink. It is a basic colouring matter, and is applied in a neutral or slightly acid dye-bath. The colour it gives is not fast to light.

*Mauve*, or *rosolan*, seems also to be related to the foregoing. It is a basic colouring matter, and is applied, therefore, in the same manner as magenta. On cotton it yields a tolerably fast violet colour.

**Induline colouring matters.** This group comprises a number of dark-blue and grey dye-stuffs very similar to each other in general pro-



perties and methods of application, *e.g.* induline, nigrosine, bleu Couplier, azo-diphenyl blue, &c. Being all sulphonic acids they are applied in an acid dye-bath, principally in wool and silk-dyeing. The colours they yield are tolerably fast to light, and have in silk-dyeing almost entirely replaced vat-indigo blues. In wool-dyeing they are less useful, chiefly because it is difficult to obtain level colours.

*Aniline black* is a colouring matter of unknown constitution, and the only important member of its class. It is not a commercial article, but has to be produced upon the fibre itself. Its application is almost entirely confined to the cotton fibre, since silk and wool, especially the latter, hinder the formation of the colour. Aniline black is a product of the oxidation of aniline. Cotton is dyed by immersing it for about two hours in a cold solution containing aniline hydrochloride, bichromate of potash, and hydrochloric acid sufficient to liberate chromic acid. Insoluble aniline black is gradually produced and largely attracted by the immersed cotton. Another method is to impregnate the cotton with a solution containing aniline hydrochloride, sodium chlorate, and vanadium or copper chloride; after drying, the fabric is rapidly steamed or passed through a heated chamber, and finally through a boiling solution of bichromate of potash and sulphuric acid. The latter method produces a black not liable to rub off, a defect which is common to the first method. A usual defect with ordinary aniline black is that it gradually assumes a greenish hue under the influence of acids (*e.g.* sulphurous acid), but this is removed if the black is highly oxidised, as for example, by passing rapidly through a boiling solution of dilute chromic acid, as described.

*Cachou de Laval* is a dyestuff produced by heating waste vegetable matter with sodium sulphide. It is employed in cotton-dyeing for producing fast shades of grey and drab. The cotton is first worked for some time in a hot concentrated alkaline solution of the colouring matter, and afterwards passed into a solution of copper sulphate, ferrous sulphate, or bichromate of potash.

**Mineral colouring matters.** This group includes chrome yellow, iron-buff, manganese brown, and Prussian blue, all of which are specially suitable for cotton-dyeing.

*Chrome yellow* is produced on cotton by impregnating the fibre with a lead salt solution, drying, and passing into a solution of bichromate of potash. The chief defects of this colour are that it is poisonous and readily affected by hydrogen sulphide.

*Iron-buff* is obtained by impregnating cotton with a ferric salt solution, and, after squeezing, passing through a solution of carbonate of soda.

*Manganese brown* is produced on cotton by impregnating the fibre with manganous chloride, passing it through dilute caustic soda, and, finally, through a dilute solution of bleaching powder in order to change the precipitated manganous hydrate into dark-brown manganic hydrate. The colour is fast to light, acids, and alkalis, but very sensitive to reducing agents, *e.g.* sulphurous acid, by which it is rapidly bleached.

*Prussian blue* is obtained by simply passing cotton dyed with iron-buff through a cold acidulated solution of potassium ferrocyanide. This colour is extremely fast to light, but readily decomposed by the action of alkalis. It is chiefly employed in cotton-dyeing, and incidentally in silk-dyeing in the production of certain blacks.

**The dyeing of mixed fabrics** of cotton and wool is carried out either by selecting those colouring matters for which both fibres have an attraction, *e.g.* the benzidine colours &c., or more usually by first dyeing the wool with an acid colouring matter in the usual manner, then mordanting the cotton with tannic acid and tartar-emetic or stannic chloride, and dyeing in the cold with a basic colouring matter. Logwood blacks are dyed by first mordanting the cotton in the cold with tannic acid and nitrate of iron, then the wool with a boiling solution of bichromate of potash, and finally dyeing both fibres thus mordanted in a hot decoction of logwood. Mixtures of cotton and silk are dyed by methods similar to those employed for cotton and wool. Fabrics of wool and silk are dyed by methods similar to those usual for wool or silk alone.

When dyeing *compound shades*, the main principle to be observed is to apply simultaneously only such colouring matters as are applicable, when used singly, by methods as similar as possible to each other. Basic and acid colouring matters ought not to be applied together in the same dye-bath, since the one requires a neutral, the other an acid bath in order to yield their full colouring power. Basic colouring matters, however, may be quite well applied to mordanted cloth along with phenolic colouring matters, since both these classes dye usually in a neutral bath.

It is very irrational to produce compound shades by the application of fast and fugitive colours; the best results are obtained by employing colouring matters of about equal fastness to various influences. If this rule is not observed the dyed colour is liable to change materially in shade under those influences to which it is subsequently submitted, *e.g.* light, washing, &c.

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J. J. H.

**DYNAMAGNITE** v. EXPLOSIVES.**DYNAMITE** v. EXPLOSIVES.

**DYSODIL.** A soft laminated carbonaceous substance of a yellowish grey or green colour, burning with a luminous flame, and a smell resembling that of burning caoutchouc. Found in Sicily and in Bavaria (Fricklinger, J. M. 1875, 760; also Church, C. N. 34, 155).









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